THE APPLICATION OF IRREVERSIBLE THERMODYNAMICS TO TRANSPORT PROCESSES IN CATION - EXCHANGE MEMBRANES

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A C K N O W L E D G E M E N T S

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SUMMARY

A study of the transport properties of normal and expanded forms of a cation exchange membrane in 0.05m calcium chloride has been carried out. Isotopic diffusion coefficients and electrical, salt diffusion and osmotic properties have been determined experimentally and the results have been used to provide an Irreversible Thermodynamic analysis of membrane phase interactions. Such an analysis is extremely rigorous and the conditions governing its validity are stated and strictly observed. In this study the properties of the ion-exchanger are defined by six phenomenological transport coefficients. Under isothermal, isobaric conditions (which were maintained for the major part of this work) only five independent equations may be formulated and so certain assumptions regarding the magnitude of one minor coefficient are necessary.

In the system described the salt uptake is small and the salt diffusional flow is predicted accurately from a knowledge of electrical conductivity, transport and transference numbers. Four sets of Onsager frictional coefficients are calculated, each using a different limiting assumption. All four assumptions have as their basis the low co-ion content of the exchanger and three of them are seen to be in good agreement for the major parameters. However, the fourth assumption, that co-ion isotope-isotope interactions are negligible, provides a set of frictional coefficients which correlates poorly with the others and so only three sets of Onsager mobility coefficients are considered.

A salt model calculation is presented which is based on the aqueous chloride solution of the membrane counterion. The model successfully predicts both the individual transport coefficients of the irreversible thermodynamic analysis and the measured transport /

transport parameters for the sodium forms of this membrane. It becomes obvious however, that there are certain significant differences between the calcium form of the membrane and the corresponding salt model (aqueous calcium chloride). Since the Salt Model Calculation for the sodium form proved successful it would appear that the differences are probably due to ion-association between the calcium and matrix-fixed charge which would lower conductivity, reduce counterion-water friction and increase interaction between counterion and matrix-fixed charge. These conclusions are strengthened by a comparison of coefficients for the sodium and calcium forms when valency differences have been accounted for.

Conductivities of mixed ionic forms (calcium and sodium) were obtained and compared with values which were predicted by assuming that the reduction of conductivity (below the ideal mixture relationship) is due to calcium-sodium interionic coupling. The theoretical model was that used successfully by Miller to predict the properties of ternary electrolyte solutions.

The predictive value of the Nernst-Planck Theory is investigated for the system described and the anomalies between calculated and observed values are rationalised by making a detailed comparison with the Irreversible Thermodynamic approach.

C O N T E N T S

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CHAPTER 1

INTRODUCTION

Ion-exchange membranes are sheets, ribbons or rods of exchange materials. These may be produced synthetically and are capable of separating two solutions. Their abilities to select and control the flow of mobile species from one solution to another renders them extremely useful. They have applications in desalination fuel cell technology and electrolyte processing. Synthetic ion-exchange materials provide a much simpler system than do natural biological membranes. A complete understanding of the transport processes of ion-exchange membranes is essential to the realisation of their full industrial potential and may also be of primary importance in the clarification of biological membrane processes.

When an ion-exchange membrane is in equilibrium with the solution of a single electrolyte four separate species exist in the exchanger phase. These are the counterion, co-ion, solvent and the matrix which includes the fixed charge. The counterion charge is of the opposite sign to the co-ions and the fixed charge. A membrane with a negative fixed charge is therefore a cation exchanger and with a positive charge an anion exchanger.

To fully comprehend the membrane transport processes a knowledge is required of the structure of the membrane and of the internal interactions between ions, matrix and solvent during such processes. Considerable difficulty is encountered, as with bead exchangers(1)(2), in obtaining a well-defined homogeneous membrane. The conclusions drawn from a detailed comparison of membranes of similar types but from different sources are therefore restricted and can be only qualitative.

In this work the transport and diffusion characteristics of

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a cation-exchange membrane in its normal and expanded forms are studied. The two membranes are very similar in capacity (per unit mass of dry matrix) and chemical constitution and differ only in geometry and consequently in solvent content and salt uptake.

The ion-exchange system under investigation is based on the graft copolymer membrane AMF C60 manufactured by the American Machine and Foundry Company, Springdale, Connecticut, U.S.A. These membranes were prepared from low-density polyethylene and contain 35% styrene and up to 2% divinylbenzene. The styrene is polymerised with chemical free-radical initiators and the membrane sulphonated with oleum. Copolymer membranes of this type are considered to be microscopically heterogeneous. They have alternative regions of crystalline polyethylene and substituted polystyrene closely intermingled to give a strong but highly permeable exchanger. The membrane itself is light brown indicating a degree of heterogeneity which is at most commensurate with the wavelength of visible light.

The membrane expands irreversibly (3) with no detectable chemical or physical deterioration when placed in water at 95°C for one hour. The transport and diffusion properties of the normal (C60N) and expanded (C60E) membranes are investigated where the counterion species is calcium and the external solution is 0.05m $CaCl_2$. The membranes were cut from adjacent areas of the original sheet and periodic checks of water content, capacity and electrical conductivity showed that the basic characteristics were constant during the course of this work.

The major portion of this thesis is concerned with an analysis of the relative values of electrical conductivity, self-diffusion, water transference, transport number and salt uptake obtained when the membranes were in 0.05m $CaCl_2$ (Osmotic flow measurements were taken when the membrane separated 0.025m and 0.075m $CaCl_2$ solutions).

Irreversible Thermodynamics, which is detailed in Chapter 2, provides /

provides a more rigorous and comprehensive analysis of these measured quantities than any other theoretical method available. This concept is however confined to situations in which the membrane system is near equilibrium and where the resultant phenomenological equations are linear functions of the applied forces. Since ion exchangers are intrinsically heterogeneous the validity of the Onsager Reciprocal Relations must be questioned (section 2.4). Many authors (4)(5)(6) have assumed such symmetry in their own systems. Snell and Stein (7) have given this problem a general treatment which is applicable to systems in mechanical equilibrium. Their conditions for the validity of the Onsager Reciprocal Relations require that flow and forces be measured normal to the membrane surface and that forces are constant over that surface. All local forces must bear a constant relationship to their potential difference across the membrane and this implies that path lengths through the membrane must be equal. These conditions are valid for a homogeneous membrane and it is postulated that the experimental membranes in this study are sufficiently homogeneous on a macroscopic scale to allow the Onsager Reciprocal Relations. Electron micrographs have shown the thorium form of AMF C60 membranes to contain local inhomogeneities consisting of regions of localised high density fixed charge which are some 200-400 Å in diameter and which are distributed closely and evenly across the membrane section (8).

A drawback of the Irreversible Thermodynamic approach is the relatively high number of independent experiments required to characterise the system. For example when the membrane is in equilibrium with a single electrolyte solution six independent equations are needed. To avoid experimental difficulties which arise when pressure and temperature gradients are used as thermodynamic forces (8)(9), studies similar to this work have been confined to isobaric/

isobaric and isothermal situations (10)(11)(12)(13). Under these conditions only five independent equations are available for the characterisation of the system described above. When isobaric and isothermal conditions are maintained several assumptions may be made in order to analyse the system using Irreversible Thermodynamics. As will be shown, these assumptions are mainly based on the relative concentrations of species in the system and as such involve several approximations concerning the relative magnitudes of the phenomenological coefficients. Although a sixth independent equation is available from self-diffusion studies the added complication of isotope-isotope interactions arises (sections 2.4.5 and 5.4). It was initially believed that for a mobile species in an ion-exchange membrane system, isotope-isotope interactions were negligible. It has subsequently been shown however (11)(14) that, for the counterion, these interactions are not only significant but the sign of the frictional coefficient is opposite to the expected. An investigation of isotope-isotope interactions has been made for the calcium form of the AMF C60 membranes and is developed later. (section 5.4)

Despite the experimental difficulties involved (8)(9) it was decided to use pressure as an additional thermodynamic force and so obtain a sixth independent phenomenological equation for the system described above. Application of a pressure gradient allows the phenomenological equations to be solved without recourse to approximations and also provides a check on the validity of the various assumptions used.

Transport and diffusion properties of normal and expanded forms of the AMF C60 membrane have been investigated thoroughly under isobaric isothermal conditions when the exchanger was in equilibrium with aqueous sodium chloride solution (particularly 0.1 m NaCl) (10).

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The results of these studies have been analysed quantitatively using Irreversible Thermodynamics and practical equations based on flows measured relative to the stationary membrane have been developed. The resultant phenomenological coefficients of the membrane electrolyte were converted to a solvent-fixed frame of reference and in situations where the membrane electrolyte uptake was essentially zero (0.1 m NaCl eqilibrium solution) they were shown to be almost identical to those of equimolal sodium chloride solutions. When these studies were extended to include situations in which the salt uptake was appreciable it was found that the observed results corresponded extremely closely with those predicted using analogous electrolyte solution (now a ternary solution) as a model (12). It was concluded that Irreversible Thermodynamics may be used to interpret and predict to a high degree of accuracy the transport and diffusion properties of the sodium form of AMF C60 membranes. The polymer matrix of polyethylene and polystyrene appeared therefore to have little or no effect upon the movement of ions or water other than the purely geometric effect of constraining these species to migrate in the membrane pores.

Nernst-Planck theory was applied to the sodium form of membrane system (12) with some success but its predictive capabilities decreased markedly as the salt uptake of the membrane increased.

The study of the transport and diffusion properties of the AMF C60 membrane when it contains a divalent counterion (calcium) is a logical extension of previous investigations. Irreversible Thermodynamics have shown that for the AMF C60 membrane in a univalent cationic form the analogous electrolyte solution is a good model on which to base predictive calculations. It is hoped to show in this work whether or not the properties of the calcium form may be analysed to a similar degree of accuracy using calcium chloride solution models.

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To ensure that as far as possible, the sodium and calcium forms of the membranes were under parallel conditions the anion concentration of equilibrium solution was the same in both cases (0.1m).

Extensive work has recently been done on membrane-solution comparisons (15) (salt model calculations chapter 6) especially for the sodium form of the membrane. This work provides an excellent basis for interpretation of the various interactions between the mobile species and will be referred to frequently.

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CHAPTER 2

Analysis of Membrane Transport Processes

Membrane transport processes may be described theoretically in three broad groups, Absolute Rate Theory, Nernst-Planck Theory and Irreversible Thermodynamics.

Absolute Rate Theory: The absolute rate theory of Eyring and co-workers (1) may be used to describe membrane transport by considering the diffusion of ions across a series of potential energy barriers. This approach has not been widely applied as the resulting equations are often complex and involve a number of parameters which are indeterminate in the membrane phase.

Nernst-Planck Theory: The classical Nernst-Planck equation (2) may be extended and used to obtain flux equations in terms of measurable parameters of the membrane and thus a predictive theory. Although these flux equations have been developed to describe diffusion in ideal solutions (in which coupling between mobile species is ignored) they have been successfully applied to membrane systems when due account has been taken of convective terms. Later in the chapter (sections 2.5.1 and 2.5.2) this theory is discussed and compared with the rigorous treatment provided by Irreversible Thermodynamics.

Irreversible Thermodynamics: Irreversible Thermodynamics (3)(4)(5)(6) is essentially phenomenological. When used to describe membrane transport processes it therefore requires the use of models to interpret the physical meaning of the coefficients obtained. This approach is completely rigorous however when applied to these membrane processes and is developed in this chapter for an ion-exchange membrane system.

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2.1 Non-Equilibrium Thermodynamics.

2.1.1 Extension of Classical Thermodynamics: Non-equilibrium thermodynamics may be applied to a system which is undergoing irreversible processes if it is assumed (7) that the system consists of an infinite number of macroscopically small sub-units which are each in local equilibrium. This assumption is valid if the system is close to equilibrium and allows local chemical potentials and partial molar quantities to be defined and governed by the laws of Classical Thermodynamics.

The second law of thermodynamics postulates the existence of entropy S. The change in entropy dS of a system undergoing an irreversible process consists of two parts (8).

$$dS = d_eS + d_iS \qquad (2.1)$$

where d_eS is the change in entropy due to a reversible interaction with the exterior and d_iS is due to the production of entropy within the system itself. The entropy change d_iS is never negative. It is zero when the system undergoes reversible changes and positive when the processes are irreversible.

$$d_iS \geqslant 0 \qquad (2.2)$$

(Equation 2.2 is a general statement of the second Law of Thermodynamics).

In an isolated system neither energy nor mass may be exchanged and so

$$dS = d_iS \geqslant 0 \qquad (2.3)$$

If such a system I is enclosed in a system II so that the total system I and II is isolated some irreversible process may take place. The entropy change would be

$$dS = dS^{1} + dS^{11} \geqslant 0 \qquad (2.4a)$$

$$= d_iS^{1} + d_iS^{11} \geqslant 0 \qquad (2.4b)$$

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In every macroscopic region in the system the entropy production due to irreversible processes is positive, so that

$$d_i S^{1} \geqslant 0 \text{ and } d_i S^{11} \geqslant 0$$

2.1.2 The Rate of Production of Entropy: The local rate of entropy production σ for each volume element dV of the system contributes to the overall entropy production rate so that

$$\frac{d_i S}{dt} = \int_V \sigma dV \qquad (2.5)$$

σ may be expressed as a sum of terms each of which is a product of a flux and a conjugate thermodynamic force. As pointed out by Meixner (9) the choice of flows or forces is to a certain extent arbitrary. However when one set of variables is chosen the set of conjugate variables is determined by the following requirements;
a) the product of any flow and its conjugate force must have the dimensions of entropy production, b) for a given system the sum of the products must remain the same for any transformation of flows and forces. In a system in mechanical equilibrium the following equation (eqn 2.6) may be applied.

$$\sigma = \frac{J_s}{T} \text{ grad } (-T) + \sum_{i=i}^{n} \frac{J_i}{T} \text{ grad } (-d\tilde{\mu}_i) + J_{ch} \frac{A}{T} \qquad (2.6)$$

where J_s, J_i and J_{ch} are the fluxes of entropy, matter and chemical reaction. The conjugate forces are defined as negative gradients of temperature T, electrochemical potential $\tilde{\mu}_i$, and affinity A of the chemical reaction.

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The dissipation function ϕ which is the rate of local dissipation of free energy by irreversible processes may be used in place of σ where

$$T\sigma = \phi \tag{2.7}$$

After some manipulation (10) equation (2.6) now becomes

$$\phi = J_s \text{ grad } (-T) + \sum_{i=i}^{n} J_i \text{ grad } (-\tilde{\mu}_i) + J_{ch}A \geqslant 0 \tag{2.8}$$

In purely diffusion processes under isothermal conditions equation (2.8) reduces to

$$\phi = \sum_{i=i}^{n} J_i \text{ grad } (-\tilde{\mu}_i) \geqslant 0 \tag{2.9}$$

Defining X_i as the thermodynamic force in joules mole $^{-1}$ cm^{-1} we have

$$X_i = \text{grad } (-\tilde{\mu}_i) \tag{2.10}$$

Equation (2.9) therefore becomes

$$\phi = \sum_{i=i}^{n} J_i X_i \geqslant 0 \tag{2.11}$$

In any practical application it is necessary to define frames of reference for the flows. The frame of reference of the flow J_i of species i (moles cm^{-2} sec^{-1}) is usually defined as relative to the local centre of mass.

2.2 Frames of Reference: Since the system under study is in a state of mechanical equilibrium equation (2.11) will apply for any frame of reference (9). In the study of membrane transport processes, flows/

flows as mentioned above, are most conveniently measured relative to the membrane and so an apparatus-fixed frame of reference is defined.

The membrane system consists of a counterion 1, co-ion 2, solvent 3 and matrix 4 so that equation (2.11) becomes

$$\phi = J_1X_1 + J_2X_2 + J_3X_3 + J_4X_4 \geqslant 0 \qquad (2.12)$$

For one dimensional isothermal diffusion the thermodynamic force X_i (equation 2.10) may be written as (11)

$$X_i = -\frac{d\tilde{u}i}{dx} = -\frac{dui}{dx} - Z_iF\frac{d\psi}{dx} - P\frac{d\tilde{V}_i}{dx} - \tilde{V}_i\frac{dP}{dx} \qquad (2.13)$$

where u_i is the concentration - dependent part of the chemical potential (joules $mole^{-1}$), Z_i is the signed valency, F is the Faraday in coulombs equivalents $^{-1}$, ψ the electrical potential in volts, P the hydrostatic pressure, $\tilde{V}_i$ the partial molar volume of the i^{th} component and x the distance parameter in cm. The term $-P\left(\frac{d\tilde{V}_i}{dx}\right)$ is negligibly small in a medium such as water which is virtually incompressible.

From the Gibbs-Duhem, $\left(\sum_i n_i\, d\mu_i = 0\right)$ equation (2.14) is easily obtained and so only n-1 forces are independent.

$$\sum_{i=1}^{4} n_iX_i = 0 \qquad (2.14)$$

where n_i is the number of moles of species i in the system. Concentration units c_i may be used and are obtained by considering n_i moles per unit volume (e.g. units of c_i moles l^{-1} may be employed). By elimination of X_4 from equations (2.14) and (2.12) the dissipation function becomes:

ϕ

$$\phi = (J_1 - \frac{c_1}{c_4} J_4) X_1 + (J_2 - \frac{c_2}{c_4} J_4) X_2 + (J_3 - \frac{c_3}{c_4} J_4) X_3 \geqslant 0 \qquad (2.15)$$

Since $J_i = c_i V_i^*$ where V_i^* is the velocity of species i relative to an arbitary frame of reference $(J_1 - \frac{c_1}{c_4} J_4)$ may be expressed as

$$(c_1 V_1^* - \frac{c_1}{c_4} c_4 V_4^*) \text{ i.e. } c_1 (V_1^* - V_4^*).$$

$V_1^* - V_4^*$ is the velocity of species 1 relative to species 4 and so $c_i (V_1^* - V_4^*)$ may be represented by J_1^4, the flow of species 1 relative to 4. Equation 2.15 may therefore be simplified to

$$\phi = J_1^4 X_1 + J_2^4 X_2 + J_3^4 X_3 = \sum_{i=1}^{3} J_i^4 X_i \geqslant 0 \qquad (2.16)$$

By a similar analysis X_3 may be eliminated from equations 2.12 and 2.14 and the flows may be defined relative to a stationary solvent (3) (equation 2.17).

$$\phi = J_1^3 X_1 + J_2^3 X_2 + J_4^3 X_4 \geqslant 0 \qquad (2.17)$$

Since, in general, membrane-fixed flows are measured and used in subsequent calculations, J_i will refer solely to flows on a membrane or 4 - fixed frame of reference. For applications which require discussion of alternative frames of reference, e.g. species k, the symbol J_i^k will be used.

2.3 Linear Phenomenological Equations and the Onsager Reciprocal Relations (O.R.R.)

Onsager showed (12) (13) that, for systems close to thermodynamic equilibrium and in a steady state, flows and forces are linearly /

are linearly related by the phenomenological equation which may be written as

$$J_i = \sum_{k=1}^{n-1} l_{ik} X_k \quad (i=1, 2, \cdots n-1) \tag{2.18a}$$

where l_{ik}, the mobility coefficients, are generalised "conductance" or "permeability" coefficients. Equation (2.18a) may be represented in matrix form (eqn. 2.18b)

$$\begin{vmatrix} J_1 \\ J_2 \\ J_3 \\ \vdots \\ J_{n-1} \end{vmatrix} = \begin{vmatrix} l_{11} & l_{12} & l_{13} \cdots & l_{1(n-1)} \\ l_{21} & l_{22} & l_{23} \cdots & l_{2(n-1)} \\ l_{31} & l_{32} & l_{33} \cdots & l_{3(n-1)} \\ \vdots & \vdots & \vdots & \vdots \\ l_{(n-1)1} & l_{(n-1)2} & l_{(n-1)3} \cdots & l_{(n-1)(n-1)} \end{vmatrix} \begin{vmatrix} X_1 \\ X_2 \\ X_3 \\ \vdots \\ X_{n-1} \end{vmatrix} \tag{2.18b}$$

The flow of the species i, J_i, is no longer solely a function of its conjugate force X_i as in the laws of Fick and Ohm for example but is modified by all other non-conjugate forces X_j to a degree which is determined by the magnitude and sign of the cross-coefficients l_{ij}.

Alternatively equation 2.18 may be written in inverse form and the independent forces of the system expressed as linear functions of the flows (14) eqn. 2.19.

$$X_i = \sum_{k=1}^{n-1} R_{ik} J_k \quad (i=1 \cdots n-1) \tag{2.19}$$

The R_{ik} coefficients obtained have the dimensions of force per unit flow and are generalised frictional or resistance coefficients.

Applying the principle of microscopic reversibility Onsager (12) showed that l- and R- coefficient matrices are symmetrical and

l_{ik} /

$$l_{ik} = l_{ki} \quad (i \neq k) \tag{2.20a}$$

$$R_{ik} = R_{ki} \quad (i \neq k) \tag{2.20b}$$

The equations (2.20) are formally known as the Onsager Reciprocal Relations (O.R.R.). These relationships reduce the number of coefficients required to characterise a system which contains j independent forces from j^2 to $\frac{j(j+1)}{2}$.

It should be noted at this stage that l- and R- coefficients are functions of the local state variables but not of the magnitude and direction of the forces (i.e. gradients) within the linear region.

It has been shown (15) that the conditions required to justify the O.R.R. experimentally are much less stringent than those imposed by the principle of microscopic reversibility.

Application of the condition for overall positive entropy production to equation 2.12 and the O.R.R. causes the cross-coefficients to be contained by the inequalities.

$$l_{ii}l_{kk} \geqslant l_{ik}^2 \tag{2.21}$$

$$\text{and } R_{ii}R_{kk} \geqslant R_{ik}^2 \tag{2.22}$$

The direct coefficients must be positive but cross-coefficients may be either positive or negative.

Since there are a variety of acceptable definitions of flows and forces which may be used to characterise a non-equilibrium system neither mobility nor frictional coefficients are uniquely specified.

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For frictional coefficients however the assumption is made that $\sum_{k=1}^{n-1} C_k R_{ik} = 0 \quad (i = 1, 2 \text{ ----- } n-1)$ (2.23)

and R_{ik} may be shown to be frame of reference independent (24).

2.4 Application of Non-Equilibrium Thermodynamics to transport processes in ion-exchange membranes: The literature contains a number of treatments of membrane transport processes using non-equilibrium thermodynamics (16)(17)(18)(19)(20).

Since ion-exchangers are inherently heterogeneous the validity of the O.R.R. must be justified (16)(19)(20). Snell and Stein (21) have applied a general treatment to systems in mechanical equilibrium. Fromthis work the conditions for the validity of the O.R.R. require that the forces and flows be measured normal to the membrane surface and that these forces must be uniform over that surface. All local forces must bear a constant relationship to the potential difference across the membrane. This means that the diffusional path lengths across the membrane must be equal. This condition implies that the local inhomogeneities of the membrane must be distributed uniformly throughout the matrix and be orders of magnitude smaller than the geometric thickness of the membrane. In effect the membrane must be uniformly heterogeneous on a "microscopic" scale or macroscopically homogeneous.

The membrane system consists of four components which are the counterion,1; the co-ion,2; water,3 and the matrix-fixed sulphonate ion,4.

2.4.1 Mobility Coefficients: The mobility coefficient approach has been used by Miller (22) to describe transport processes in binary solutions (solvent-fixed frame of reference). It has however been found to be very useful when applied to membranes since it produces relatively simple equations for observed transport properties (e.g. specific conductivity and transport number).

From equation 2.15 it can be seen that three phenomenological equations are required to characterise the system. These may be derived from equation 2.18 where n=4. The l_{ik} coefficient matrix may therefore be solved only if the results of six independent experiments are obtainable. When isobaric and isothermal conditions are observed only electrical and chemical potential forces may be used in this system. A theoretical treatment of the experiments available using these two forces under steady state conditions will now be considered. The phenomenological equations for this system are (2.18)

$$\begin{aligned} J_1 &= l_{11} X_1 + l_{12} X_2 + l_{13} X_3 \\ J_2 &= l_{21} X_1 + l_{22} X_2 + l_{23} X_3 \\ J_3 &= l_{31} X_1 + l_{32} X_2 + l_{33} X_3 \end{aligned} \qquad (2.18)$$

2.4.1.1. Electrical Potential Gradients: If an electrical force is applied to an isothermal isobaric system in the absence of a chemical potential gradient, X_1 and X_2 are determined solely by electrical potential gradients and X_3 is zero. Therefore from equation 2.13

$$X_i = Z_i F \left\{ \frac{-d\psi}{dx} \right\} \qquad (i = 1,2)$$
$$X_3 = 0$$

Under these conditions, conductivity, transport number and electro-osmotic experiments may be carried out.

2.4.1.1.a./

2.4.1.1.a Conductivity: The current density (amp cm^{-2}), I, passing through the membrane may be written as

$$I = (Z_1 J_1 + Z_2 J_2) F \qquad (2.24)$$

However, since the phenomenological equations 2.18 may be simplified to

$$J_1 = l_{11} X_1 + l_{12} X_2$$

$$J_2 = l_{21} X_1 + l_{22} X_2$$

$$J_3 = l_{31} X_1 + l_{32} X_2$$

equation 2.24 may be altered using equations 2.18 and 2.13 to

$$I = F^2 \left\{ - \frac{d\psi}{dx} \right\} (Z_1^2 l_{11} + 2 Z_1 Z_2 l_{12} + Z_2^2 l_{22}) \qquad (2.25)$$

By Ohm's Law

$$I = K \left\{ - \frac{d\psi}{dx} \right\} \qquad (2.26)$$

From equations 2.25 and 2.26 the relationship

$$K = \alpha F^2 \qquad (2.27)$$

is therefore obtained where

$$\alpha = (Z_1^2 l_{11} + 2 Z_1 Z_2 l_{12} + Z_2^2 l_{22}) \qquad (2.28)$$

2.4.1.1.b Transport Number: The transport number t_i on a given frame of reference is defined as the fraction of the total current carried by that ion. It can be written as

$$t_i = \frac{Z_i F J_i}{I} \qquad (2.29)$$

As an example the counterion and co-ion transport numbers t_1 and t_2 may /

may be obtained by substituting in equation 2.29, for I using equation 2.25, for J_1 and J_2 using equations 2.18, and for X_1 and X_2 using equation 2.13. The resulting expressions become

$$t_1 = (Z_1^2 l_{11} + Z_1 Z_2 l_{12})/\alpha \qquad (2.30a)$$

and

$$t_2 = (Z_2^2 l_{22} + Z_1 Z_2 l_{12})/\alpha \qquad (2.30b)$$

2.4.1.1.c Electro-osmosis: The transference number of a species is defined (23) as the number of moles of the species transferred by one Faraday of electricity through a stationary cross-section in the direction of positive current. The expression obtained for water is therefore

$$t_3 = \frac{J_3 F}{I} \qquad (2.31)$$

and from equations 2.31, 2.25, 2.18 and 2.13,

$$t_3 = \frac{Z_1 l_{13} + Z_2 l_{23}}{\alpha} \qquad (2.32)$$

2.4.1.2 Chemical Potential Gradient Applied: When two solutions of differing concentrations are separated by a membrane a chemical potential gradient is set up across the membrane which results in salt diffusion, osmotic flow and a membrane potential. In this situation there is no electric current and the corresponding forces are the sum of chemical and electrical current. The zero net current condition is represented by equation 2.33,

$$I = (Z_1 J_1 + Z_2 J_2) F = 0 \qquad (2.33)$$

Therefore /

Therefore

$$Z_1 J_1 = - Z_2 J_2 \qquad (2.34a)$$

or

$$\frac{J_1}{r_1} = \frac{J_2}{r_2} = J_s \qquad (2.34b)$$

where r_1 and r_2 are the stoichiometric coefficients for ionisation and J_s is the salt flow.

There are severe limitations on the use of this method to obtain l- and R- coefficients for the membrane phase because the coefficients are a function of the intensive parameters of the system such as concentration. Since the concentration varies across the membrane the coefficients obtained by experiment will be an average value. Results of significance will therefore be obtained only if the concentration difference on either side of the membrane is small and linear gradients of chemical potential can be assumed.

The concentration gradient provides a thermodynamic force X_i so that from equation 2.13

$$X_i = \left\{ - \frac{d\tilde{\mu}_i}{dx} \right\} = \left\{ - \frac{d\mu_i}{dx} \right\} + Z_i F \left\{ - \frac{d\psi}{dx} \right\} \qquad (i=1,2)$$

$$\text{and } X_3 = \left\{ - \frac{d\mu_3}{dx} \right\}$$

Evaluation of J_1 and J_2 in equation 2.33 using phenomenological equations (2.18) will provide the expression 2.35

$$(Z_1 l_{11} + Z_2 l_{21})X_1 + (Z_1 l_{12} + Z_2 l_{22})X_2 + (Z_1 l_{13} + Z_2 l_{23})X_3 = 0 \qquad (2.35)$$

Using equations 2.30 and 2.32 with equation 2.35 the relationship 2.36 is obtained,

$$\frac{t_1}{Z_1} X_1 + \frac{t_2}{Z_2} X_2 + t_3 X_3 = 0 \qquad (2.36)$$

and /

and à combination of equations 2.13 and 2.36 gives the equation 2.37,

$$F\left\{-\frac{d\psi}{dx}\right\} = \frac{t_1}{Z_1}\left\{\frac{d\mu_1}{dx}\right\} + \frac{t_2}{Z_2}\left\{\frac{d\mu_2}{dx}\right\} + t_3\left\{\frac{d\mu_3}{dx}\right\} \qquad (2.37)$$

Equation 2.37 may be integrated across the whole membrane to obtain the diffusion potential and this may be used to calculate $\left\{-\frac{d\mu_1}{dx}\right\}$ and $\left\{-\frac{d\mu_2}{dx}\right\}$ as shown in appendix A.1. The diffusion flows of salt (J_s) and water (J_3) may be calculated using the equations above.

2.4.1.2.a <u>Osmotic Flow:</u> Equation (2.18) may be expanded using the equations 2.13 and 2.37 to obtain the expression for the osmotic flow J_3

$$J_3 = \left\{l_{13} - \frac{t_1}{Z_1}\alpha t_3\right\}\left\{-\frac{d\mu_1}{dx}\right\} + \left\{l_{23} - \frac{t_2}{Z_2}\alpha t_3\right\}\left\{-\frac{d\mu_2}{dx}\right\}$$

$$+ \left\{l_{33} - t_3^2\alpha\right\}\left\{-\frac{d\mu_3}{dx}\right\} \qquad (2.38)$$

The chemical potential of the salt (μ_{12}) is given by

$$\mu_{12} = r_1\mu_1 + r_2\mu_2 \qquad (2.39)$$

where r_1 and r_2 are the stoichoimetric coefficients for ionisation, it can be seen that

$$\frac{1}{r_1}\left\{l_{13} - \frac{t_1}{Z_1}\alpha t_3\right\} = \frac{1}{r_2}\left\{l_{23} - \frac{t_2}{Z_2}\alpha t_3\right\} \qquad (2.40)$$

Using equations 2.39 and 2.40 equation 2.38 becomes

$$J_3 = \frac{1}{r_1}\left\{l_{13} - \frac{t_1}{Z_1}\alpha t_3\right\}\left\{-\frac{d\mu_{12}}{dx}\right\} + \left\{l_{33} - t_3^2\alpha\right\}\left\{-\frac{d\mu_3}{dx}\right\} \qquad (2.41)$$

For the system described in this thesis, J_3 has the same sign as $\left(-\frac{du_3}{dx}\right)$ while it is opposed by $\left(-\frac{du_{12}}{dx}\right)$. $l_{33}\left(-\frac{du_3}{dx}\right)$ indicates the direct effect of a force causing a flow of water while the term $-t_3^2\alpha\left(-\frac{du_3}{dx}\right)$ represents the drag from the ions in the system. The term $\left(l_{13} - \frac{t_1}{z_1}\alpha\, t_3\right)\left(-\frac{du_{12}}{dx}\right)$ represents the reduction in water-flow caused by salt-water coupling.

2.4.1.2.b Salt Flow: As mentioned above (section 2.4.1.2.) salt flow J_s for an electrolyte may be written as

$$J_s = \frac{J_1}{r_1} = \frac{J_2}{r_2} \tag{2.34b}$$

and it is possible to express J_s in a form similar to J_3 by substituting equations 2.13 and 2.37 into equation 2.18 to provide the expression

$$J_s = \frac{J_1}{r_1} = \frac{1}{r_1}\left\{\left(l_{11} - \frac{t_1^2}{z_1^2}\alpha\right)\left(-\frac{du_1}{dx}\right) + \left(l_{12} + \frac{t_1}{z_1}\frac{t_2}{z_2}\alpha\right)\left(-\frac{du_2}{dx}\right) + \left(l_{13} - \frac{t_1}{z_1}t_3\alpha\right)\left(-\frac{du_3}{dx}\right)\right\} \tag{2.42}$$

It can be shown that

$$\frac{1}{r_1^2}\left(l_{11} - \frac{t_1^2}{z_1^2}\alpha\right) = \frac{1}{r_1 r_2}\left(l_{12} - \frac{t_1 t_2}{z_1 z_2}\alpha\right) = \frac{-z_1 z_2}{r_1 r_2}\left(\frac{l_{11}l_{22} - l_{12}^2}{\alpha}\right) \tag{2.43}$$

Using the expressions 2,43 and 2.39, equation 2.42 now becomes

$$J_s = \frac{-z_1 z_2}{r_1 r_2}\left(\frac{l_{11}l_{22} - l_{12}^2}{\alpha}\right)\left(-\frac{du_{12}}{dx}\right) + \frac{1}{r_1}\left(l_{13} - \frac{t_1 t_3}{z_1}\alpha\right)\left(-\frac{du_3}{dx}\right) \tag{2.44}$$

In this case J_s will have the same sign as $\left(-\frac{du_{12}}{dx}\right)$ while it will be opposed to $\left(-\frac{du_3}{dx}\right)$.

The second term is the indirect effect of a force on water (X_3) upon/

upon the net salt flow and is due to coupling between the salt and water.

Equations 2.41 and 2.44 represent a redefinition of flows and forces for a salt-water system. The phenomenological equations which would arise in the system of salt, s, and water would be,

$$J_s = L^1_{ss} X_s + L^1_{s3} X_3 \qquad (2.45a)$$

$$J_3 = L^1_{3s} X_s + L^1_{33} X_3 \qquad (2.45b)$$

It can be seen by referring to equations 2.41 and 2.44 that the O.R.R. is still preserved.

Since only five independent equations 2.30a, 2.30b, 2.32, 2.41 and 2.44 are available to describe the system the number of independent experiments which can be performed under isobaric and isothermal conditions is immediately limited to five.

2.4.2 Hyperfiltration Studies: It has been shown that under isobaric and isothermal conditions only five independent equations may be constructed to evaluate six unknown quantities. If however a pressure gradient is applied across the membrane in the absence of electrical forces a sixth equation is immediately available. The procedure used is called "reverse osmosis" (25) and in order to assure that no current is flowing the apparatus is built so that there is no metal connection between the high and low pressure side solutions. If the applied pressure and high concentration remain constant the fluxes (and therefore the low concentration) remain constant, thus ensuring against interfacial polarisation.

X_3 may be evaluated using equation 2.13

$$X_3 = -\frac{du_3}{dx} + \tilde{V}_3 \left\{ -\frac{dP}{dx} \right\} = +\frac{RT}{d} \ln \left\{ \frac{a'_3}{a''_3} \right\} + \tilde{V}_3 \left\{ -\frac{\Delta P}{d} \right\}$$

where/

where a_3 is the activity coefficient of water, d is the membrane thickness, and indices ' and " represent feed (f) and product (p) solution.

$$\text{Since } \ln a_3 = \frac{-r' w_a}{10^3} \; \phi_s m_s \qquad (2.46)$$

Where r is the number of ions in one molecule of solute, w_a is the molecular weight of solvent, and ϕ_s and m_s are the osmotic coefficient and molality respectively of the solution.

X_3 therefore becomes,

X_3 = Applied force - osmotic force

$$= \frac{P-P^o}{d} - \frac{r RT w_a}{d10^3} \cdot \left\{ \phi_f m_f - \phi_p m_p \right\} \qquad (2.47)$$

where $P-P^o$ is the difference between applied pressure and standard state pressure. (1 atm. at 25°C).

2.4.3. Frictional or R-coefficient Approach: When equation 2.19 is applied to the 4-component system under investigation it becomes,

$$X_i = \sum_{k=1}^{3} R_{ik} J_k \qquad (i=1,2,3)$$

It may be shown using procedures similar to those detailed above for the mobility coefficients that the equations obtained for electrical forces are

$$\frac{Z_1 F^2}{K} = \frac{t_1}{Z_1} R_{11} + \frac{t_2}{Z_2} R_{12} + t_3 R_{13} \qquad (2.48a)$$

$$\frac{Z_2 F^2}{K} = \frac{t_1}{Z_1} R_{21} + \frac{t_2}{Z_2} R_{22} + t_3 R_{23} \qquad (2.48b)$$

$$0 = \frac{t_1}{Z_1} R_{31} + \frac{t_2}{Z_2} R_{32} + t_3 R_{33} \qquad (2.48c)$$

and/

and for salt diffusion due to chemical potential gradients,

$$X_1 = R_{11}J_1 + R_{12}J_2 + R_{13}J_3 \qquad (2.49a)$$

$$X_2 = R_{21}J_1 + R_{22}J_2 + R_{23}J_3 \qquad (2.49b)$$

$$X_3 = R_{31}J_1 + R_{32}J_2 + R_{33}J_3 \qquad (2.49c)$$

However the application of equations 2.34b and 2.39 to equation 2.49 produces the two equations,

$$X_{12} = (r_1^2R_{11}+r_2^2R_{22}+r_1r_2(R_{12}+R_{21}))J_s + (r_1R_{13}+r_2R_{23})J_3 \qquad (2.50a)$$

$$X_3 = (r_1R_{31} + r_2R_{32})J_s + R_{33}J_3 \qquad (2.50b)$$

Five independent equations therefore result which contain six unknowns and again a complete analysis of the system cannot be achieved. Since the relationship (2.23) provides a value for R_{4k} nine independent equations may be constructed in terms of R-coefficients. These equations are still not completely soluble as they contain ten unknowns.

A disadvantage of the R-coefficient approach is that no simple equations may be derived to describe the flows, J_s or J_3, explicitly in terms of their forces. Neither can simple equations be constructed for conductivity, transport or transference numbers individually. There are however three main advantages which the R-coefficient approach has over that of the l-coefficient. Firstly the R-coefficients can be interpreted physically as a parallel to mechanical friction (2.4.4). Secondly, as discussed previously, the R-coefficients are frame of reference independent. Lastly and also as a consequence of equation 2.23, a value of R_{4k} may be obtained which is a measure of the frictional interaction between the mobile species and the matrix, 4.

2.4.4 Spiegler Approach: The phenomenological equations which Spiegler derived (17) are based on the concept of frictional interaction. It is suggested that the thermodynamic driving force on a substance in/

in the steady state is equal in magnitude and opposite in direction to the sum of the frictional forces between i and all other species. Considering the thermodynamic force on the counterion X_1 in this system we therefore have,

$$X_1 = -F_{12} - F_{13} - F_{14} \tag{2.51}$$

where F_{12}, F_{13} and F_{14} are the frictional forces between the counterion and the coion, water and matrix respectively. However, from equation 2.19 in this system is

$$\begin{aligned} X_1 &= R_{11}J_1 + R_{12}J_2 + R_{13}J_3 \\ &= c_1R_{11}\bar{V}_1^* + c_2R_{12}\bar{V}_2^* + c_3R_{13}\bar{V}_3^* \end{aligned} \tag{2.19}$$

where the frame of reference of the vector quantities is membrane-fixed. Equation 2.23 gives

$$c_1R_{11} = - c_2R_{12} - c_3R_{13} - c_4R_{14} \tag{2.23}$$

By combining equations 2.19 and 2.23 the relationship

$$X_1 = c_2R_{12}\,(\bar{V}_2^* - \bar{V}_1^*) + c_3R_{13}\,(\bar{V}_3^* - \bar{V}_1^*) + c_4R_{14}\,(0 - \bar{V}_1^*) \tag{2.52}$$

is obtained. Comparing equations 2.15 and 2.52 it is seen that generally

$$F_{ik} = - c_kR_{ik}(\bar{V}_k^* - \bar{V}_i^*) \tag{2.53}$$

If $\bar{X}_{ik}$ is the frictional coefficient between one mole of species i and the total concentration of k around it in the membrane phase, then (24)

$$R_{ii} = \frac{\sum \bar{X}_{ik}}{c_i} \tag{2.54a}$$

$$\text{and } R_{ik} = R_{ki} = - \frac{\bar{X}_{ik}}{c_k} = - \frac{\bar{X}_{ki}}{c_i} \quad (i \neq k) \tag{2.54b}$$

The summation indicated in equation (2.54a) is carried out over all species in the membrane. It is apparent from (2.54b) that the O.R.R. does not hold for $\bar{X}_{ik}$ and for this reason frictional coefficients are usually calculated in terms of R_{ik}.

The/

The concept of (mechanical) friction has been used to interpret transport processes observed in the system. Spiegler has described his model in terms of mechanical friction which must be taken at a molecular level to apply to the retardation of particles due to collision with other particles. Since this approach always produced a positive value for $\overline{X}_{ik}$ he pointed out the limitations of this analogy because R_{ik} can be either positive or negative. Kedem (27) has in fact suggested this change of sign of R_{ik} by considering that the R coefficients between attracting species are negative and between repulsing species are positive, which is generally observed of solutions (22)(29) although this scheme of signs is not obeyed in all cases in membranes, and specific examples are cited in two earlier publications (30)(31).

2.4.5 Tracer Diffusion and Isotope - Isotope Interactions: No approach has, as yet, been discussed whereby a complete analysis of the system being studied may be achieved under isobaric and isothermal conditions. Investigations of the two most promising treatments namely those of the l- coefficients and R- coefficients has in each case yielded five independent equations which contain six unknown. In early studies Spiegler (17) and Meares (32) and others have however used isotopic diffusion measurements to provide further information by assuming that isotope - isotope interactions were negligible. This assumption has however been proved to be misleading (33)(34) for counterion and water isotope - isotope interactions. Kedem and Essig (35) have used local values of the frictional coefficients (r_{ij}) to obtain eqn(2.61). These coefficients may be integrated across the total thickness of the membrane to provide a relationship between them and an isotopic diffusion coefficient D_{ii}, as shown

D_{ii} /

$$D_{ii} = \frac{RT}{c_i (R_{ii} - R_{ii'})} \qquad (2.55)$$

where R,T, and c_i are the gas constant, absolute temperature and concentration of species i(mol cm^{-3})respectively.

The term $c_i R_{ii}$ measures the total frictional contribution between one mole of i and all other species in the system per unit volume, while $c_i R_{ii'}$ is the frictional contribution between one mole of isotope i' and the bulk i per unit volume. If Spiegler's approximations were therefore applicable a sixth independent equation would be immediately provided to complete the evaluation of frictional coefficients since $R_{ii'}$ would then be negligible.

The relationship above (equation 2.55) was derived by relating the flows (J_i) of the species (i) under test to their driving forces (X_i) and coupled flows. Then the following phenomenological equations may be written for any local region of the exchanger in which 1 denotes the bulk ion and 1' is a tracer. The assumption that 1 and 1' are separate ionic species must be made.

$$X_1 = r_{11}J_1 + r_{11'}J_{1'} + \sum_{i=2,3} r_{1i}J_i \qquad (2.56a)$$

$$X_{1'} = r_{1'1}J_1 + r_{1'1'}J_{1'} + \sum_{i=2,3} r_{1'i}J_i \qquad (2.56b)$$

$$X_j = r_{j1}J_1 + r_{j1'}J_{1'} + \sum_{i=2,3} r_{ji}J_i \quad (j = 2,3) \qquad (2.56c)$$

In a self-diffusion experiment there are by definition no gradients across the membrane other than that of the radioactive isotope concentration. The experimental details of self - diffusion study will be discussed later (section 39). $X_1, X_{1'}, J_1$ and $J_{1'}$, will therefore be the only non-zero forces and fluxes in equations 2.56 so that those equations become,

$$X_1 = r_{11}J_1 + r_{11'}J_{1'} \qquad (2.57a)$$

$X_{1'}$ /

$$X_{1'} = r_{1'1}J_1 + r_{1'1'}J_{1'} \qquad (2.57b)$$

$$0 = r_{j1}J_1 + r_{j1'}J_{1'} \quad (j = 2,3) \qquad (2.57c)$$

Since the net current in the system is zero,

$$J_1 + J_{1'} = 0 \qquad (2.58)$$

Under the conditions stated the thermodynamic force X_i (equation 2.13) reduces to

$$X_i = \left\{ -\frac{d\tilde{u}_i}{dx} \right\} = RT\left\{ -\frac{d \ln c_i}{dx} \right\} = \frac{RT}{c_i} \left\{ -\frac{dc_i}{dx} \right\} \qquad (2.59)$$

so that by substituting equations (2.58) and (2.59) into equation 2.56a the expression,

$$\frac{RT}{c_1} \left\{ -\frac{dc_1}{dx} \right\} = (r_{11} - r_{11'}) J_1 \qquad (2.60a)$$

is obtained i.e.

$$J_1 = \frac{RT}{c_1(r_{11} - r_{11'})} \cdot \left\{ -\frac{dc_1}{dx} \right\} \qquad (2.60b)$$

However, since Ficks first law of diffusion states that the flux and its conjugate force are related thus

$$J_1 = \mathcal{d}_{11} \left\{ -\frac{dc_1}{dx} \right\} \qquad (2.61)$$

comparison of equation 2.60b and 2.61 produces the expression

$$\mathcal{d}_{11} = \frac{RT}{c_1 (r_{11} - r_{11'})} \qquad (2.62)$$

Integration of equation 2.62 across the membrane as a whole gives the form of equation 2.55 corresponding to ion 1. That is

$$D_{11} = \int \frac{RT}{c_1 (r_{11} - r_{11'})} = \frac{RTd}{c_1 R^x} \qquad (2.63)$$

where R^x is known as the exchange resistance and d is the membrane thickness.

The validity of several other relationships which rely on the measurement of tracer fluxes in the presence of isotope-isotope interaction have been examined theoretically by Kedem and Essig

(35) /

(35). Their most important conclusion from the point of view of these studies is that the relationship

$$\text{Net flux} = \text{Influx} - \text{Outflux} \tag{2.64}$$

remains true whether or not there is isotope interaction.

Another expression derived by these authors for the flux rates in the presence of isotope interaction states that

$$\ln(f) = \ln\left(\frac{\text{forward flow}}{\text{back flow}}\right) = \frac{JR^x}{RT} \tag{2.65}$$

where J is the net flow and f is the flux ratio. When equation 2.24 (where J_i may be the net flow of ion i) is substituted along with equation 2.50 into equation 2.65 the usual form of the flux ratio expression results,

$$\ln(f) = \frac{t_i I d}{Z_i D_{ii} c_i F} \cdot \tag{2.66}$$

2.5.1 Nernst-Planck Equations: The total flux J_i of a species i in an ion exchanger in isothermal isobaric conditions is due to the influence of three factors. It will therefore consist of three components (36)

1. J_i (diff) which is the flux caused by the chemical potential gradient.
2. J_i (el) which is the flux due to the electrical potential gradient.
3. J_i (con) which is the flux caused by convection.

The flux J_i(diff) is related to the chemical potential u_i of species i by the equation,

$$J_i(\text{diff}) = -D_{ii} c_i \ \text{grad.}\ u_i \tag{2.67}$$

and also J_i(el) may be written in terms of the electrical potential gradient thus,

$$J_i(\text{el}) = -u_i' z_i c_i \ \text{grad}\,\psi \tag{2.68}$$

In equation 2.68 u_i' is the electrochemical mobility of species i and may be related to the diffusion coefficient of i (D_{ii}) by the Nernst-Einstein equation which is/

Nernst-Einstein equation which is,

$$u_i' = \frac{D_{ii}F}{RT} \qquad (2.69)$$

Combination of equations 2.68 and 2.69 therefore results in the expression,

$$J_i(el) = - D_{ii}Z_ic_i \frac{F}{RT} \quad \text{grad}\,\psi. \qquad (2.70)$$

The third flux listed, which is caused by convection due to the coupling of counter ions and solvent, results directly from the frame of reference being membrane-fixed. It is represented by the equation

$$J_i(con) = c_i\nu \qquad (2.71)$$

where ν is the rate of motion of the centre of gravity of the pore liquid.

The total flux J_i may therefore be represented by summing equations 2.67, 2.70 and 2.71 to obtain

$$J_i = -D_{ii}c_i \left(\text{grad}\, u_i + \frac{Z_iF}{RT} \text{grad}\,\psi\right) + c_i\nu \qquad (2.72)$$

In the absence of a chemical potential gradient the equation 2.72 simplifies to

$$J_i = - Z_ic_iD_{ii} \frac{F}{RT} \text{grad}\psi + c_i\nu \qquad (2.73)$$

In order however that equation 2.73 holds true for the ion exchange system under investigation three main assumptions must be made:

a. The Nernst-Einstein relation (equation 2.69) which is strictly true only for ideal solutions may be used in a membrane situation. Although an ion-exchange system would seem to be far removed from that of an ideal solution this assumption has proved to be fairly good (rigorous) in practice. It is therefore argued that the smallness of the pores in the membrane prevents formation of ionic clouds (37) which are known to deform under the influence of an electric field and thus contribute to deviations from the Nernst-Einstein relationship in a non-ideal system.

b. Only /

b. Only coupling between fluxes produced by convection are considered .

c. Convection carries all species at the same rate (i.e. there is no differential retardation of the mobile species).

When the rate of motion (ν) of the centre of gravity of the pore liquid is investigated it is found that,

$$\nu = \frac{Z_4 F c_4}{P_o V_w} \text{ grad } \psi = Z_4 U_3' \text{ grad } \psi \qquad (2.74)$$

where $U_3' = Fc_4 / P_o V_w$ is the mobility of the pore liquid, P_o is the specific flow resistance of the exchanger, V_w is the fractional pore volume and Z_4 is the signed valency of the fixed ions. The value of U_3' may be obtained using the definition,

$$J_3(el) = Z_4 c_3 U_3' \text{ grad } \psi \qquad (2.75)$$

and a combination of equations 2.27, 2.31 and 2.32 so that on rearranging,

$$U_3' = - \frac{t_3 K}{c_3 F Z_4} \qquad (2.76)$$

Since the electrical current density I may be expressed by the relationship, $I = F \sum_i Z_i J_i$ (eqn 2.24), the equation,

$$I = F \sum_i \left(-Z_i^2 c_i D_{ii} \frac{F}{RT} + Z_4 U_3' c_i Z_i\right) \text{ grad } \psi \qquad (2.77)$$

may be obtained by inserting equations 2.73 and 2.74 into 2.24.

Application of the condition of overall electroneutrality in the membrane,

$$\sum_i c_i Z_i = 0 \quad (i=1,2,4) \qquad (2.78)$$

to equation 2.77 produces the expression

$$I = F \left\{ \sum_{i=1,2} \left(-Z_i^2 c_i D_{ii} \frac{F}{RT}\right) - Z_4^2 c_4 U_3' \right\} \text{ grad } \psi \qquad (2.79)$$

Substitution of equation 2.76 into 2.79 yields

$$I = \left\{ F \sum_{i=1,2} \left(-Z_i^2 c_i D_{ii} F/RT\right) + Z_4 c_4 t_3 K / c_3 \right\} \text{ grad } \psi \qquad (2.80)$$

The equations 2.27, 2.29 and 2.80 may be combined to form equations /

equations which predict values for K and t_i in terms of D_{ii}, D_{22} and t_3 and these predictions are compared with the experimental values obtained. The resulting expressions become

$$K = \frac{F^2}{RT} \left(\frac{\sum_i z_i^2 c_i D_{ii}}{1 + z_4 c_4 t_3/c_3} \right) \tag{2.81}$$

and $$t_i = \frac{F^2 z_i^2 c_i D_{ii}}{RTK} + \frac{t_3 c_i z_i}{c_3} \tag{2.82}$$

2.5.2 Comparison of Non-Equilibrium Thermodynamics and Nernst-Planck Equations: In the derivation of the Nernst-Planck equations several assumptions must be made for the system (the most important ones are discussed in the previous section.) The validity of these assumptions may be discussed more easily by expressing the Nernst-Planck equations in a non-equilibrium thermodynamic form and comparing the result with this completely rigorous approach.

The phenomenological equations for an electrical gradient only in the system discussed are

$$J_1 = (z_1 l_{11} + z_2 l_{12}) F \text{ grad } (-\psi) \tag{2.83a}$$

$$J_2 = (z_1 l_{21} + z_2 l_{22}) F \text{ grad } (-\psi) \tag{2.83b}$$

and may be compared with the Nernst-Planck equations,

$$J_1 = \left(z_1 \frac{c_1 D_{11}}{RT} + \frac{c_1}{c_3} \frac{t_3 K}{F^2} \right) F \text{ grad } (-\psi) \tag{2.84a}$$

$$J_2 = \left(z_2 \frac{c_2 D_{22}}{RT} + \frac{c_2}{c_3} \frac{t_3 K}{F^2} \right) F \text{ grad } (-\psi) \tag{2.84b}$$

Since J_3 has been used in the derivation of U_3' and is therefore implicit in equations 2.84 the equations for J_3 need not be considered here. Equations 2.84 can be seen to contain their corresponding self-diffusion coefficients and these must firstly be expressed in terms of l- coefficients before any analogies may be drawn between equations 2.83 /

2.83 and 2.84. The self-diffusion coefficient D_{ii} of species i has however been obtained in terms of R-coefficients in section 2.45 (as a result of non-equilibrium thermodynamics being applied to the self diffusion process) and it is equally straightforward to use l-coefficients instead thus obtaining the expression,

$$D_{ii} = RT \left(\frac{l_{ii}}{c_i} - \frac{l_{ii}'}{c_i'} \right) \qquad (2.85)$$

Where l_{ii}' is the isotope-isotope mobility coefficient and c_i' is the concentration of traced ion i.

Since, as will be reasoned later in a discussion section (5.5), $\frac{l_{22}'}{c_2'}$ is negligible compared with $\frac{l_{22}}{c_2}$ equations 2.84 will become, using equations 2.27 and 2.32,

$$J_1 = \left(Z_1 l_{11} + \frac{c_1}{c_3}\left(Z_1 l_{13} + Z_2 l_{23}\right) - \frac{Z_1 c_1 l_{11}'}{c_1'}\right) F \operatorname{grad}(-\psi) \qquad (2.86a)$$

$$J_2 = \left(Z_2 l_{22} + \frac{c_2}{c_3}\left(Z_1 l_{13} + Z_2 l_{23}\right) - \frac{Z_2 c_2 l_{22}'}{c_2'}\right) F \operatorname{grad}(-\psi) \qquad (2.86b)$$

Comparing equations 2.83a and 2.83b with 2.86a and 2.86b shows,

$$Z_2 l_{12} = \frac{c_1}{c_3}\left(Z_1 l_{13} + Z_2 l_{23}\right) - \frac{Z_1 c_1}{c_1'} l_{11}' \qquad (2.87a)$$

$$Z_1 l_{21} = \frac{c_2}{c_3}\left(Z_1 l_{13} + Z_2 l_{23}\right) - \frac{Z_2 c_2}{c_2'} l_{22}' \qquad (2.87b)$$

Equations 2.87a and 2.87b show that if isotope-isotope interactions are neglected the l_{12} cross-coefficient of equations 2.83a and 2.83b is replaced by a weighted fraction of l_{13} and l_{23} in equations 2.86a and 2.86b. Since in the system c_1 is much larger than c_2 this fraction will cause J_1 to be corrected to a much greater extent than J_2 and will consequently destroy the O.R.R.. Investigation of equations 2.86 ,however, reveals that the isotope-isotope interaction term, although neglected by the Nernst-Planck, acts in the opposite sense/

sense to the l_{13}, l_{23} term. Although it does not necessarily follow from this observation that the isotope term would restore the O.R.R. the comparison of J_1 with J_2 would certainly be improved.

CHAPTER 3

Experimental

3.1 Preparation of Electrolyte Solutions: All solutions were prepared from analar salts and high quality distilled water using grade A calibrated volumetric apparatus. Alkali chloride solutions of specified molarity were prepared directly by weight from the salt which had been dried at 120°C in a desiccator containing phosphorous pentoxide.

Stock solutions of calcium chloride were initially obtained to an approximate molarity, however, and later analysed for calcium by complexometric titration (38) using E.D.T.A. and Eriochrome-Black T indicator. These stock solutions were diluted to the concentrations needed for equilibration procedures. This refinement was required because calcium chloride crystals were deliquescent and an accurate preparation by weight could not be made.

3.2 Radioactive Isotopes and Counting Methods: Radioactive isotopes tritium, calcium - 45 and chlorine - 36 were required for capacity, salt uptake and transport and diffusion studies on the membrane species. These were obtained in microcurie amounts from the Radiochemical Centre, Amersham.

Calcium - 45, in the form of aqueous calcium chloride and tritiated water were used directly after stock dilution. Chlorine - 36 was obtained as aqueous sodium chloride which was converted to calcium chloride by ion - exchange on the calcium form of Amberlite IR 120 sulphonic acid resin.

A small ion - exchange column about 10 cm. long was constructed using a calculated amount of the ion - exchange resin described above. The resin bed was column - washed with distilled water then dilute hydrochloric /

hydrochloric acid and finally with distilled water to ensure that the exchange resin was in the hydrogen form and non - exchanged acid removed. The exchange column was then converted to its calcium form with an appropriate quantity of calcium chloride and used, as required to obtain $CaCl_2^{36}$ by passing a specified quantity of $NaCl^{36}$ carefully and slowly down the column.

Radioactive samples were counted using an Automatic Liquid Scintillation Spectrometer (Nuclear Chicago Mark 1).

Samples of radioactive solutions were taken using Hamilton Microlitre Syringes fitted with Chaney adapters. With these syringes it was possible to extract samples of between 0.08 and 0.4 ml. which were reproducible in volume to $\pm$ 0.1%. The radioactive samples were counted in standard scintillation vials of volume 20 ml. and containing 10 ml. of dioxan phosphor solution (39) which was totally miscible with the aqueous samples used.

Since all vial samples from each experiment were identical apart from the varying quantities of radioactive isotope present, no corrections were required for differential quenching effects.

Standard scintillation counting procedures were used and "background" counts on a series of vials were made for each counting experiment. A typical sample was counted for twenty minutes to ensure that a total count of about 10^4 c.p.m. or more was obtained. After correction for "background" the counting reproducibility was found to be in the range $\pm$ 1 - 2%. However, since tritium is a low energy beta emitter, it was counted with a lower efficiency so that the counting reproducibility decreased to about $\pm$ 3%.

3.3 Membrane Samples: The membranes studied were A.M.F. C60 cation exchangers manufactured by the American Machine and Foundry Company, Springdale /

Springdale, Conn., U.S.A. These graft copolymer membranes are prepared from low - density polyethylene and contain 35% styrene and up to 2% divinyl benzene. The styrene is polymerised with chemical free - radical initiators and the membrane is sulphonated with oleum. This type of membrane is considered to be microscopically heterogeneous having alternate regions of crystalline polyethylene and substituted polystyrene intermingled.

Arnold and Koch (40) found that these membranes expand irreversibly showing no chemical or physical deterioration, when heated in water at 95°C for 1 hour.

It has been shown recently (41) that the degree of expansion of these membranes varies markedly with length of heating time, and with temperature.

In order to obtain a degree of expansion similar to that described by Gardner (30) a sample of membrane sheet was placed in water at 95°C for thirty minutes. During this treatment the sheet became slightly opaque and expanded both in thickness and in area.

3.4 Preconditioning: Discs of membrane approximately 3.8 cm. in diameter were cut from the normal and expanded sheets. Both sets of normal (C60N) and expanded (C60E) membranes were subjected to a number of preconditioning cycles as described by Helfferich (42). The membranes were treated, each for some hours, in turn with methanol, 1M hydrochloric acid, distilled water, 1M sodium hydroxide and distilled water. The methanol was used to remove any monomer or similar material while the hydrochloric acid and sodium hydroxide removed any acid - or base - soluble impurities resulting from manufacture.

The membranes were converted to the sodium form by successive equilibrations /

equilibrations with 1M sodium chloride for a minimum of four days and then placed in distilled water to leach out sorbed electrolyte. The weight of the leached sodium form of the membrane was determined as described later (Section 3.5). The cycling process was continued until the membrane wet weights were constant.

At this stage the membranes were in the sodium form because their properties were ultimately to be compared with earlier studies (43)(44) which were concerned with this form. Physical parameters of the C60N and C60E membranes were measured as described. The two C60N and the two C60E membranes which corresponded most closely to those described in previous studies (43)(44) were used in the following investigations.

Conversion to different ionic forms was made by successive equilibrations over a period of five days with the chloride salt of the metal ion which was required as counterion..

3.5 Wet Weights: The membrane loses water rapidly after its surface has been blotted dry and so a dynamic method was used to obtain wet weights.

The membrane was removed from the equilibrating solution using forceps and placed between two"hard" filter papers. Since the solution on the surface of the membrane saturated the filter paper adjacent to it, it was assumed at that stage that no moisture apart from surface solution had been removed from the membrane itself. The membrane was quickly blotted and a stop-clock was started immediately. When its surface was absolutely moisture free the membrane was transferred with dry forceps to a small weighed wire stirrup suspended in a balance. The weight of the membrane (plus frame) was noted at fifteen second intervals for some two minutes. Since the weight loss was found to be linear /

linear over this time (about one milligram is lost every fifteen seconds from a membrane weighing about 0.3 grams) the true wet weight of the membrane was obtained by extrapolation to zero time from the graph of weight against time.

The membrane was returned to its equilibrating solution and this weighing procedure was repeated several times. Weights were reproducible to $\pm$ 0.1%.

3.6 Dry Weights: The leached membrane was placed in a dry weighing bottle in a desiccator containing phosphorous pentoxide. The desiccator was evacuated, sealed and maintained at 40°C for several days. The membrane was then removed and weighed in a stoppered weighing bottle to determine its dry weight. The process was repeated until a constant dry weight was obtained.

The membrane disc was then re-equilibrated with the test solution and its wet weight was redetermined to ensure that the drying and reswelling process was reversible.

3.7 Physical Dimensions:

3.7.1. Diameter: The membrane was removed from its equilibrium solution and placed, still wet, between two thick optically flat glass plates. The diameter of the membrane was then measured using the micrometer stage of a projection microscope (Nikon Profile Projector model 6C). The measurement was made several times and across several diameters of the test disc to obtain an average value. The micrometer could be read to an accuracy of $\pm$ 0.0001 cm. but because of irregularities on the edge of the membrane, measurements were only reproducible to $\pm$ 0.05% on a diameter of about 3.5 cm.

3.7.2. /

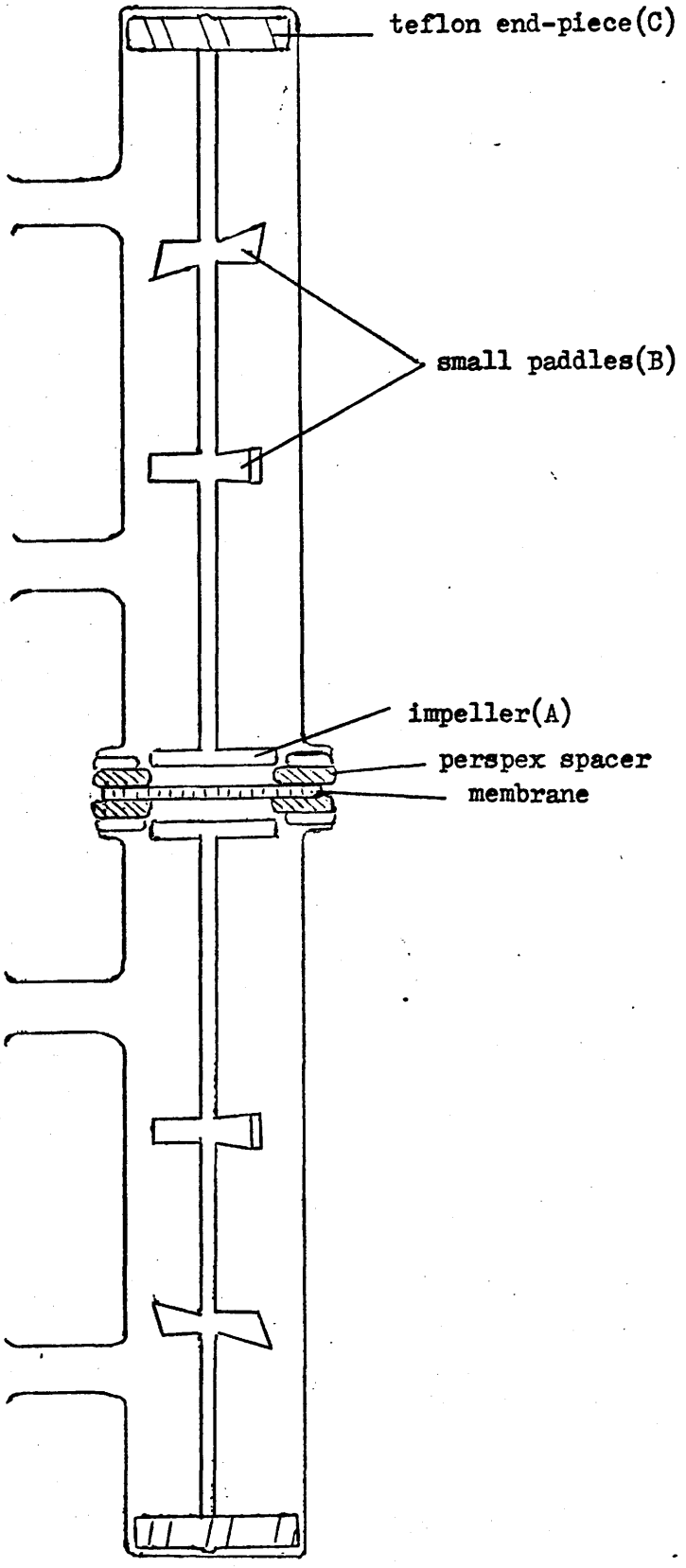
3.7.2. Thickness: The wet membrane was placed between two optically flat microscope cover plates (measuring about one centimetre square) and the total thickness was measured at many locations on the surface of the disc using a micrometer screw gauge.

Using this method a membrane thickness of some 0.03 cm. may be obtained to ± 1.0% and any deviations in the thickness over the surface were found to be well within this error.

3.8 Concentration of Ions in Membrane Phase: The membrane was equilibrated for twenty-four hours in 20 ml. of its equilibrium solution which had been labelled with the appropriate radioactive isotope. It was then blotted and to ensure that all the radioactive solution had been removed from its surface it was dipped momentarily, using clean forceps, in either an inactive sample of the equilibrium solution (for co-ion capacity determination) or pure distilled water (e.g. for counterion capacity determination). The last step was most important when, as in co-ion capacity determination, the amount of radioactive isotope in the membrane was small. The amount of radioactivity remaining on the surface would then have been large compared to the traced ion content of the disc. The membrane was blotted once more, immersed in 20 ml. of the inactive solution and allowed to re-equilibrate for twenty-four hours. Five samples were then removed by syringe from both radioactive solutions and counted as described previously (Section 3.2)

The procedure was repeated twice more and the concentration of traced ion in the membrane was calculated as described (Appendix A.2). The results for the counterion concentration were reproducible to ± 1.0%. However, the co-ion capacity being only 1% of that of the counterion /

Figure 3.1



DIFFUSION CELL

counterion is determined to a lower degree of accuracy so that results for this determination are reproducible to ± 5%.

3.9 Tracer Diffusion: Rates of diffusion of the radioactive tracers were measured in a cell similar to that described by Mackay and Meares (45) and shown in figure 3.1.

A teflon paddle assembly lay along each half-cell. It consisted of an impeller (A) situated some 1 - 2 m.m. from the exposed surface of the membrane, a small paddle (B) positioned half-way along the teflon shaft and a small bar magnet (C) imbedded in the teflon end-piece. The paddle system was driven by an external master magnet connected by gears to a Citenco electric motor which operated from a stabilised voltage source. A constant stirring speed was maintained throughout the experiment and measured directly using a Dawe 1200E stroboscope to an accuracy of ± 1%.

The volume of each half-cell was about 60 ml.

The membrane was placed between two identical perspex spacers which were pinned together so that the aperture in the centre of each corresponds exactly on either side of the membrane. The two half-cells were then clamped together to sandwich the spacers as shown and both half-cells were filled simultaneously from burettes to prevent the membrane from bulging under unequal pressure. Assembly and filling of the cell were carried with as little delay as possible to minimise water loss from the membrane because a partially dry membrane when clamped on the cell was found to buckle slightly on reswelling.

When the cell had been filled it was checked especially in the region of the membrane to ensure that it contained no air bubbles and was leak free. As a further precaution against leaking the joints between the half-cell and the spacers were sealed with a thin layer of paraffin /

paraffin wax. The cell was then immersed in a water bath at 25 ± 0.05C° up to the level of the sample inlets and, when at least thirty minutes had elapsed to allow the assembly to come to thermal equilibrium, stirring was commenced.

To begin the diffusion experiment the solution in one side of the cell was traced with a calculated quantity of the appropriate radioactive isotope and the time noted.

The samples were again removed using calibrated Hamilton microlitre syringes fitted with Chaney adaptors. 0.08ml. samples were removed and counted as described previously. The activity of the inactive side was corrected for errors caused by the sampling procedure as shown in Appendix A.3. The diffusion runs were performed at a stirring speed of 550 r.p.m.

A plot of activity against time gave a straight line to indicate that the system was in a steady state and therefore easily characterised. A study of other membrane systems (31) has revealed that before a steady state was reached a considerable delay has occurred during which concentration profiles were established at the exchanger (This "dead time" may be treated by the non-steady method of Meares (46)). Results obtained for the system under investigation, however have revealed that "dead time" is so short that it is undetectable within the limits of experimental error. These limits are discussed later in the section. The gradient of the graph was used to calculate a self-diffusion coefficient, $\overline{D}_A$, for a particular isotope from the relationship (equation 3.4) derived as follows (47).

The isotopic flux in the steady state may be represented by

$$J = \overline{D}_A \overline{c}' / d \qquad (3.1)$$

where J is the isotopic flux in moles cm^{-2} sec^{-1}, $\overline{c}'$ is the membrane tracer concentration on the active side and d is the membrane thickness.

The /

The indices ' and " refer to the active and inactive sides respectively.

Mass balance in the system is indicated by

$$qJ = V'' \, dc''/dt \qquad (3.2)$$

where q is the area of the membrane (cm^2) through which diffusion occurs, V" is the volume of the solution on the initially inactive side (cm^3) and dc"/dt is the rate of increase in activity on the inactive side.

If interfacial resistance is zero so that each side of the membrane is in equilibrium with its adjacent solution then,

$$\frac{\bar{c}'}{\bar{c}} = \frac{c'}{c} \quad \text{and} \quad \frac{\bar{c}''}{\bar{c}} = \frac{c''}{c} \qquad (3.3)$$

where c is the bulk concentration of the traced ion in the external solution (mole cm^{-3}) and $\bar{c}$ is the bulk concentration of the same ion in the membrane (mole cm^{-3}).

Substituting for J from equation (3.1) and $\bar{c}'$ from equation (3.3) into equation (3.2) gives, on rearranging,

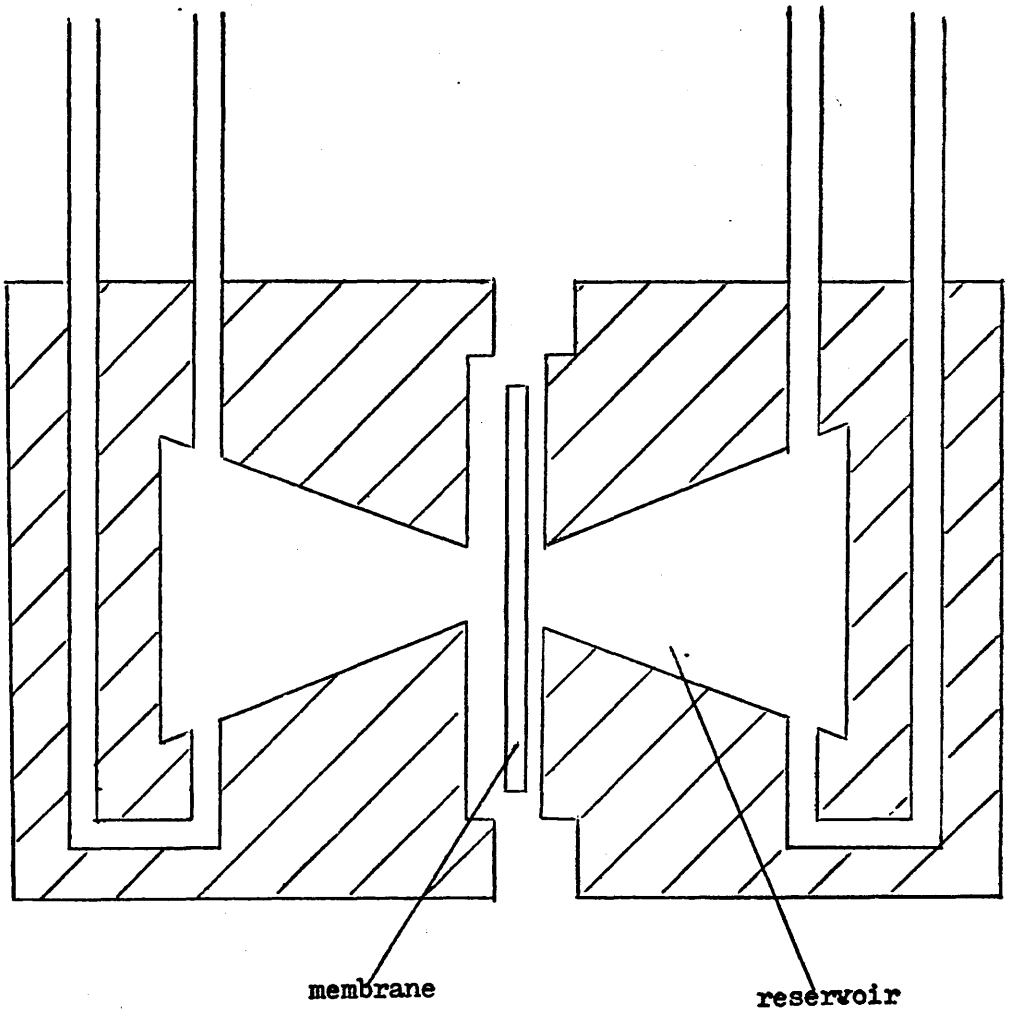
$$\bar{D}_A = \frac{V'' \; c \; d \; dc''/dt}{c' \; \bar{c} \; q} \qquad (3.4)$$

This equation is applicable only if c' remains constant (within the limits of counting error) throughout the experiment. In the event of c' changing significantly, however, equation (3.4) is modified to (45)

$$\bar{D}_A = \frac{V'' \; c \; d}{\bar{c} \; q} \cdot \frac{d \; (c''/c')}{dt} \qquad (3.5)$$

The above calculation derives an expression for the apparent diffusion coefficient but takes no account of the region of liquid at each membrane-solution interface which will remain unstirred no matter how /

Figure 3.2



CONDUCTIVITY CELL

how efficiently the bulk solution is agitated. Scattergood and Lightfoot (34) have shown that the thickness of the unstirred film is a function of stirring speed and have calculated a true diffusion coefficient $\bar{D}$ as shown in appendix A.4. It was discovered however that in the system under study, as in others (30)(31), only counterion self-diffusion coefficients were corrected significantly. The correction used did in fact consistently increase the counterion self-diffusion coefficient by about 4% while the calculated percentage error was no greater than $\pm$ 2% except for tritium diffusion where the reduced efficiency of the counting produced an error of $\pm$ 3%.

3.10 Membrane Conductivity: The conductivity of the membrane was determined using an indirect method (34)(48)(49) which involved measuring the conductivity of the membrane plus a known volume of solution.

A Wayne Kerr B331 conductivity bridge capable of an accuracy up to $\pm$0.01% was used to measure the conductivity between the electrodes of the high precision cell shown in figure 3.2 and described in the U.S. Manual for Testing Permselective Membranes (50). The cell was designed so that it contained the same volume of solution whether or not the membrane was present. Since the membrane contains a high concentration of counterions relative to its equilibrium solution it will display a much higher electrical conductivity. In order, therefore to increase its resistance relative to that of the whole cell and thus increase the accuracy of the results obtained the membrane area exposed was very small (0.09855 cm^2) compared to the disc's area (10 cm^2).

When the cell had been assembled it was filled with solution carefully ensuring that no air bubbles remained inside it.

The /

The cell was next placed on a thin polythene bag. When the assembly was positioned in an oil bath maintained at 25 ± 0.01°C the bag collapsed around the cell thus allowing good thermal contact while preventing the conductivity apparatus from being contaminated with the thermostat fluid. Thermal equilibrium was indicated by constant conductivity readings.

The cell was then dismantled, the membrane under investigation was placed in position as shown in figure 3.2 and the assembly and filling process was repeated. Conductivity was measured as above and the resistance of the membrane was found by subtraction.

Since the exposed area of the membrane was much smaller than its total area two problems were encountered. Firstly, the area under study may not have been representative of the membrane as a whole. To investigate this possibility a number of membranes were cut from the same sheet and examined. All were found to have conductivities within 1% of the mean value. As a further precaution, one expanded C60E and one normal C60N membrane were each trimmed to a smaller diameter and resistance determined for each at different positions over the membrane surfaces. Again the conductivities observed were within 1% of the mean value.

Secondly, conduction paths through the cell aperture other than normal to the exposed area were considered. The measured resistance values were corrected for these edge effects using the theoretical treatment given by Barrer (51). This correction when applied lowered the specific conductivity by some 4%.

The main source of error in this experiment arose when very dilute solutions (less than 0.1 molar) were being used. The resistance of the membrane and solution was then so near that of the solution itself that the reproducibility of the measurements decreases from ± 1% for /

for solutions of over 0.1M to about ± 1.5% for solutions of 0.05M or less.

The method described has several advantages over direct methods described in the literature (40) (45) (52) (53) (54). These procedures involve measuring the resistance between two electrodes in direct contact with a membrane strip. The problem of unknown interfacial resistances set up by these methods must therefore be overcome by measuring the membrane resistance at various points along its length. and calculating the true value by subtraction. If the membrane is anisotropic different conductivities will result. The main disadvantage of these methods lies in the fact that the measurements are being made along the length of the membrane whereas all other properties are measured normal to the membrane surface.

3.11 Diffusion with a Concentration Gradient - Salt Flow: The flow of electrolyte through the membrane under the influence of a salt concentration gradient was measured by monitoring the co-ion tracer flux. The membrane was clamped into the cell which was assembled and filled as described in tracer diffusion studies (section 3.9) except that the solutions on either side of the membrane differed in concentration. These solutions were allowed to come to a steady state of diffusion by leaving the cell for twenty-four hours under the previously described isothermal conditions (section 3.9) and were renewed before beginning the experiment.

A calculated amount of chlorine - 36 was added to the half-cell containing the more concentrated solution and the diffusion process was monitored as described for isotopic diffusion studies (section 3.9). After re-equilibrating the membrane with inactive solution the experiment was repeated with the isotope now in the dilute solution.

The /

The rate of flow of co-ion tracer with and against the concentration gradient was therefore obtained and the net salt flow calculated.

The flow of salt across the membrane was determined for a calcium chloride concentration gradient of 0.025/0.075 molal and the results were found to be reproducible to $\pm 3\%$.

3.12 Transport Numbers: Since the A.M.F. C60 membranes used in this work were found to exclude co-ions efficiently it was expected that the counterion transport number would be very close to unity. It was therefore decided to determine the transport number of the co-ion.

Many transport studies have been made using the classical Hittorf method (55) and subsequent analysis of electrolyte in the anode and cathode compartments of the cell. This approach has however proved to be inaccurate particularly when dilute solutions have been used because of the high current densities required.

Membrane potential measurements (55) have also been used to determine an average transport number. These measurements are done using a concentration cell in which the ion-exchange membrane separates two solutions of different concentration. If the electrodes are reversible to the anion the e.m.f. of the cell (E) may be given by the expression (49) (56) (57) (58),

$$E = \frac{3}{2} t_1 \frac{RT}{F} \ln \frac{a''_{\pm}}{a'_{\pm}} + t_3 \frac{RT}{F} \ln \frac{a''_3}{a'_3}$$

(derived as shown in appendix A.1) where R, T and F are the gas constant, absolute temperature and a Faraday respectively, $a''_{\pm}$ and $a'_{\pm}$ are the activities of concentrated and dilute solution respectively

and/

and t_3 is the water transference number. t_1, the transport number of the counterion, is an average value since the concentration of solution on either side of the membrane is different. If the concentration difference is small the transport number obtained should be a good estimate of the value corresponding to the mean of the two concentrations. However if the concentration difference is lowered the e.m.f. will decrease and the percentage error in measuring it will increase. Also the accuracy of the value of activities a' and a" will become extremely important.

The method used in these studies to obtain the transport number involves the use of radioactive tracers to determine the flow of co-ion tracer with and against the electric current. The bulk flow of co-ion, J_2, may be calculated from the net flow of radioactive tracer and may be used to calculate the transport number of the co-ion, t_2, from equation (2.29).

$$t_2 = \frac{Z_2 F J_2}{I} \qquad (2.29)$$

The cell used in the experiment was similar to that used in tracer diffusion studies (section 3.9) except that it was fitted with two circular platinum mesh electrodes situated about 3 cm. on either side of the membrane and parallel to it. These electrodes were silver plated from a solution of potassium argentocyanide (59). The silver on one electrode was then converted almost entirely to silver chloride by electrolysis in 0.1 molar hydrochloric acid. If too much silver chloride is deposited on an electrode it tends to flake off easily and so the number of coulombs used in the electrolysis is limited. (The electrode could be used conveniently to pass 60 coulombs of electricity.) /

electricity.)

The cell was assembled, filled and allowed to achieve thermal equilibrium as described in section 3.9. The assembly was connected to a constant current source (Solartron A.S.1413) so that the silver chloride electrode was the cathode. The solution in the anode compartment was traced with the radioactive isotope chlorine - 36. The circuit was closed and a current was passed until most of the chloride was transferred from cathode to anode (about 45 minutes at a current density of 4 mA cm^{-2}). The current was monitored using a Solartron digital voltameter which measured the potential drop across a standard resistor. The flow of co-ion tracer was determined as described in the diffusion experiments. When the anode had been almost entirely chloridised the current was reversed and the experiment was repeated. This time chlorine - 36 was being removed by oxidation at the anode and a correction for this dilution was applied as described in Appendix A.5.

The flow of radioactive isotope both with and against the electric current were determined in the same experiment and therefore under identical experimental conditions.

To prevent polarisation the current density was never allowed to exceed 4 mA cm^{-2}.

Two expressions which are derived in the previous chapter (equations 2.29 and 2.66) may be used to calculate the transport number of the co-ion from the flux measurement obtained. In equation 2.29 the net flow J_2 of ion (which is the difference between the flows measured with J_i' and against J_i'' the current) is used to obtain the transport number t_i of that ion as shown (where $J_i = J_i' - J_i''$).

$$t_i = \frac{z_i F J_i}{I} \qquad (2.29)$$

where /

where Z_i is the valency of the ion F is a Faraday and I is the current density (amps cm^{-2}).

The transport number of ion i may also be calculated using the rates of the fluxes measured with and against the current using the equation (2.66)(35)(60),

$$\frac{(J_i^{\prime})}{(J_i^{\prime\prime})} = \frac{t_i \, I \, d}{Z_i \, F \, c_i \, D_{ii}} \qquad (2.66)$$

where $J_i^{\prime}$ and $J_i^{\prime\prime}$ are the fluxes with and against the current, c_i is the concentration of species i in the membrane, D_{ii} is its membrane self-diffusion coefficient and d is the membrane thickness. It can be seen immediately that two separate experiments must be performed to obtain a value of t_i from equation 2.66. One experiment must be done to find the net flow of species i and one to find the diffusion coefficient D_{ii}. Unless both experiments are done under identical conditions a source of error is produced. It was found that the ratio of the flows produced by current density used was always in the order of 1:1 to 1:2 and this resulted in an accuracy of only some $\pm$ 10 to 12% being obtained for the co-ion transport numbers when calculated from eqn. 2.66. It was therefore decided to use equation 2.29 to calculate the transport number values although, because the net flow was much smaller than either forward or backward flow this equation could still only produce results reproducible $\pm$ 8%.

3.13 Osmosis: The cell was assembled as described for the salt flow studies (section 3.11). For osmotic experiments, however, a right-angled capillary was fitted to one inlet in each half-cell so that the calibrated stem of each was horizontal during the course of the experiment. The solutions which completely filled each half-cell and

part //

part of the calibrated capillary stem had been degassed to ensure absorption of air bubbles which had not been removed during the filling process. Leakage from the B10 inlets of the cell was prevented by applying a thin layer of silicon grease to the surfaces of contact of these inlets with the capillaries and stoppers and by fitting these capillaries and stoppers with B10 teflon sleeves.

These experiments were performed under the same conditions as the salt flow measurements so that the same concentration gradient existed across the membrane and a steady state of diffusion was again attained.

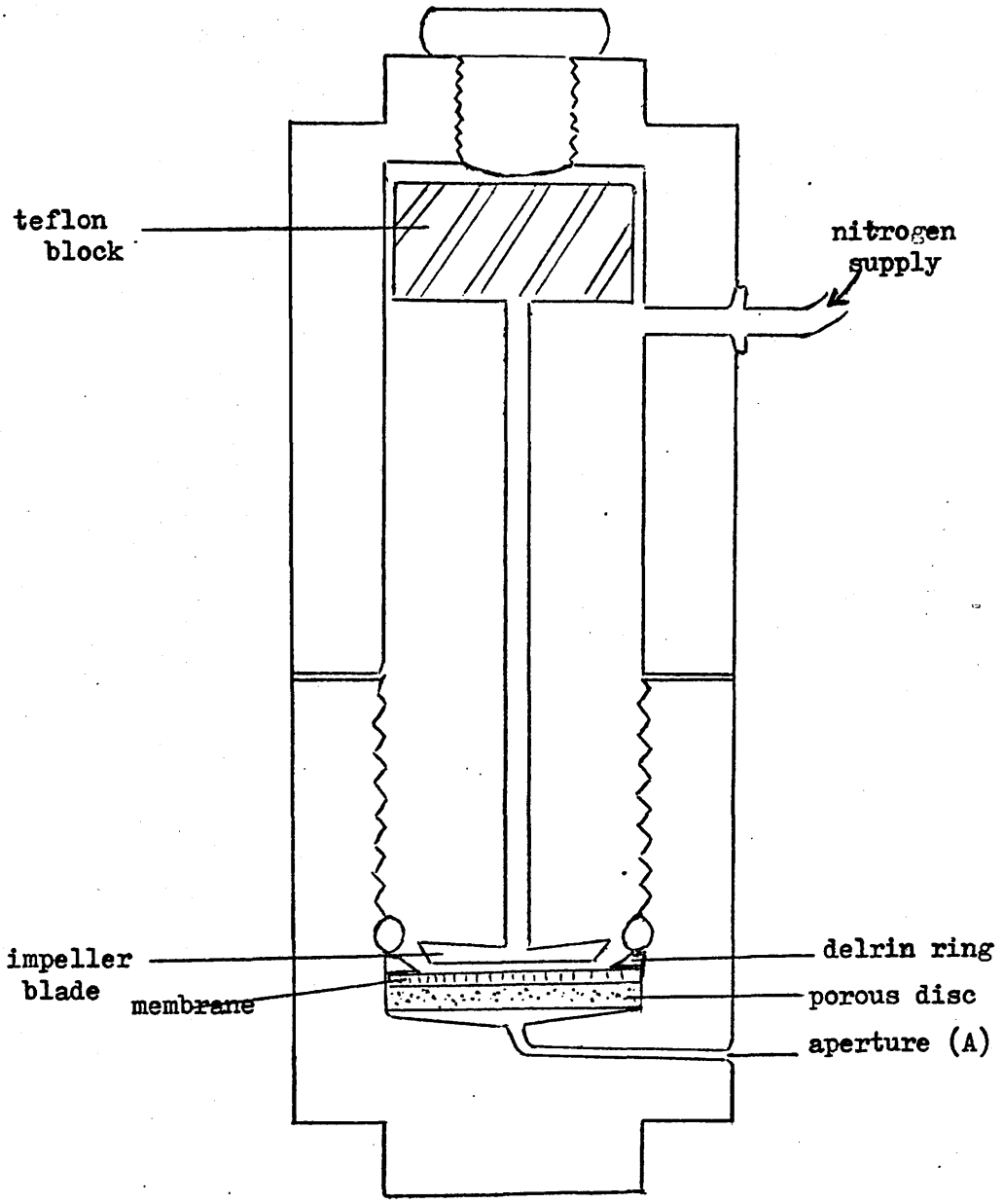
The osmotic flow was measured by monitoring the capillary readings with time. The time scale for all the experiments performed in this work was about thirty-six hours. The flow rate for the concentration gradient used (0.025m/0.075m) was found to be reproducible to $\pm 3\%$.

3.14 Electro-osmosis Experiments: Electro-osmotic experiments were performed using the transport number cell which was fitted with right-angled capillaries plus teflon sleeves as described in section (3.13) and filled with a degassed solution. The assembled cell was immersed up to the sample inlets in a thermostat maintained at 25 $\pm$ 0.01°C and allowed to come to thermal equilibrium.

When the capillary readings were steady (indicating that the cell was leak-free and at thermal equilibrium) the current was passed through the membrane and the capillary reading again monitored with time. The current was then reversed and the experiment repeated.

Equation (2.31) was then used to calculate the water transference number t_3 from the net flow of water J_3 (moles $cm^{-2}sec^{-1}$) which was obtained from the measured flow of solution in the capillary. The/

Figure 3.3



HYPERFILTRATION CELL

The rate of flow of water was measured under the influence of three different current densities (1 mA cm^{-2}, 4 mA cm^{-2}, 9 mA cm^{-2}). It was found that in the absence of a polarisation effect the transference number was independent of current density and was reproducible to $\pm$ 1%.

3.15 Hyperfiltration: The cell used for hyperfiltration studies was constructed of Delrin and designed and set up as shown. (fig. 3.3).

The paddle assembly in the cell consisted of a cylindrical teflon block containing a small bar magnet and an impeller blade which were connected with a teflon rod and was driven by magnetic coupling.

The membrane was positioned on a porous disc in the lower part of the cell and clamped in place by a Delrin ring which defined the exposed area of the membrane and a rubber oaring. The two parts of the cell were screwed tightly together and filled with the appropriate solution via the inlet at the top. The assembled cell was allowed to come to thermal equilibration overnight in an air thermostat maintained at 25 $\pm$ 0.2%.

Stirring was started and after ensuring that the paddle assembly was being rotated efficiently the stopper at the top of the cell was replaced and the nitrogen source connected as shown. The nitrogen cylinder valves were adjusted so that a pressure of 400 p.s.i. was maintained throughout the experiment. This pressure was monitored using a Budenberg gauge (which could be read to an accuracy of $\pm$ 0.5% full scale deflection).

A small weighed collecting tube was connected by means of a short capillary to the aperture (A) below the membrane. The glass-Delrin joint was coated with silicon grease to prevent leakage. The weight /

weight of product solution collected was noted for a given time interval (usually about 24 hours) so that the rate of flow of solution through the membrane could be calculated and expressed in grams per unit time. The collected solution was then analysed to discover its concentration. This could be done in two ways:

1) the conductance of the solution was measured accurately and its concentration found directly from an already prepared graph of concentration against specific conductance.

2) the solution was titrated potentiometrically against standard silver nitrate solution to discover the concentration of chloride ions present.

An alternative method was also used to measure the rate of flow solution through the membrane. The collecting tube was replaced by a calibrated capillary and the joints again greased. The rate of flow of solution along the capillary was then found by using a stop-clock.

It was found however that the cylinder valves could maintain a steady pressure to an accuracy of only $\pm$ 5% over the experimental time. Consequently the reproducibility of the concentration and rate measurements for consecutive runs was considerably less than the accuracy of each individual concentration and rate measurement.

CHAPTER 4

Results and Discussion.

4.1 Physical Properties: The general physical characteristics of both normal (C60N) and expanded (C60E) AMF C60 cation exchange membranes in the calcium form are tabulated below (table 4.1). The membrane discs selected for this study were chosen for their similarity when in the sodium form to the C60N and C60E membranes studied previously (43)(44). For example, comparison of the membrane discs used in this work with those studied by Gardner and Paterson (43) shows that the expanded forms, C60E in particular, have very similar water contents (% water with respect to dry matrix used in this work is 75.9% while that used by Gardner and Paterson contained 77.7% water).

4.1.1 Water Content: The ability of a membrane to swell and accommodate solvent is determined by the elastic resistance of the matrix as a whole.

It is evident from table 4.2 that the water content of both normal and expanded forms of the membrane decreased when the sodium counterion was replaced by calcium. The percentage weight of water with respect to the weight of dry matrix was found to be 27.1% for the C60N and 61.6% for the C60E membrane when the equilibrium solution was 0.05m $CaCl_2$. When the same membranes were in equilibrium with 0.1m NaCl their corresponding water contents were 36.1% and 75.9% respectively. The water content of the C60 membranes described in section 4.1 (43) were 52.6% and 77.7% in 0.1m NaCl and henceforth these will be the membranes referred to when comparisons are made between the calcium and sodium forms of the AMF C60.

It should be noted that these comparisons are made when the membranes are in equinormal equilibrium solutions. Unless otherwise stated /

TABLE 4.1

General Physical Properties of the A.M.F. C60 membranes in 0.05m $CaCl_2$.

	C60N	C60E
Dry weight (g)	0.2453	0.1896
Wet weight	0.3118	0.3064
Weight water (g)	0.0665	0.1168
% water w.r.t. dry weight	27.11	61.6
Radius (cm)	1.72	1.74
Thickness (cm)	0.028	0.031
Volume (cm^3)	0.260	0.295
c_1, (m.mol/ml of membrane)	0.437	0.426
c_2, (m.mol/ml of membrane) x 10^3	3.14	6.83
c_3, (m.mol/ml of membrane)	14.28	22.08
c_4, (m.mol/ml of membrane)	0.871	0.846

TABLE 4.2

Tortuosity factors and water content comparisons.

External solution	0.1m NaCl		0.05m $CaCl_2$	
Membrane	C60N	C60E	C60N	C60E
% water w.r.t. dry weight	36.0	75.9	27.1	61.6
V_w	0.277		0.257	0.397
θ_m	6.22		6.78	4.04
θ_p	4.99		5.44	3.23

V_w is defined as the volume fraction of pore liquid in the exchanger.

stated these equilibrium solutions are 0.05m $CaCl_2$ and 0.1m NaCl.

At the membrane-solution interface there is local equilibrium between water (solution) and water in the membrane so that the chemical potentials of water in solution and in the membrane are equal, $u_3 = \bar{u}_3$, where barred symbols represent membrane functions. Equilibrium is maintained by a differential pressure higher in the membrane than in solution $(\bar{P} - P)$ so that,

$$u_3 + RT \ln a_3 = \bar{u}_3 + RT \ln \bar{a}_3 + (\bar{P} - P)\,\bar{V}_3. \qquad (4.1)$$

The standard states for water taken as pure at 298.16 K are equal in both phases $(u_3 = \bar{u}_3)$. a_3 is the activity for water and $\bar{V}_3$ the partial molal volume of water.

From eqn (4.1),

$$RT \ln \frac{a_3}{\bar{a}_3} = (\bar{P} - P)\,\bar{V}_3 \qquad (4.2)$$

where $(\bar{P} - P)$ is the swelling pressure. The swelling pressure is therefore a function of the water activity in the solution, a_3, as well as of that in the membrane. The swelling pressure cannot be calculated in general, but Helfferich (2) has evaluated it in particular cases with exchanger beads which were selected within the range of about 1% to 16% divinylbenzene thus representing a considerable range of degree of crosslinking.

Work done on the C60N membrane shows that the swelling pressure varies considerably as the cation in the equilibrium solution and therefore the counterion is changed. Table 6.5 shows that the percentage water with respect to weight of dry matrix decreases as the atomic weights of the alkali earth metal ions increase.

4.1.2 Electrolyte/

4.1.2 Electrolyte Uptake: The concentrations of ions in the membranes were determined by the method of isotopic distribution described in section 3.8. These concentrations are expressed in millimoles per millilitre of membrane (table 4.1).

It is noted that the counterion concentration c_1 of the expanded membrane is slightly lower than that of the normal (0.426 mmol ml^{-1} compared with 0.437 mmol ml^{-1}). This was to be expected since the concentration (or density) of fixed-charge per millilitre of membrane must decrease as the membrane expands.

In both membranes the concentration of co-ion c_2 is a small fraction (about 1%) of c_1. Reference to table 4.1 shows that c_2 is 3.14×10^{-3} mmol ml^{-1} of membrane for the C60N membrane. A Donnan potential exists at the membrane-solution interface and tends to exclude co-ions from the membrane. This potential is reduced in the expanded form C60E and the electrolyte uptake increases. The Donnan potential may also be used to explain why the uptake of co-ion is much larger when the membranes are equilibrated with calcium chloride than with equinormal sodium chloride (c_2 values for the C60N and C60E membranes in 0.1M sodium chloride are lower, 2.4×10^{-3} and 5.2×10^{-3} mmol ml^{-1} of membrane respectively).

It is found quite generally in studies with sulphonated exchangers (61) that electrolyte exclusion is more efficient with counterions of low valency and co-ions of high valency; thus Na_2SO_4 is more strongly excluded by a cation exchanger than NaCl but as observed here NaCl is more strongly excluded than $CaCl_2$.

4.2 Isotopic Tracer Diffusion: The tracer diffusion coefficients of counterion, co-ion and water were measured for the calcium forms of both/

TABLE 4.3

Water Self Diffusion and Tortuosity factors.

	C60N	C60E
D_{33}(cm. sec^{-1}) x 10^6	5.03	6.79
D_{33}° / D_{33}	4.35	3.23
θ_m	6.78	4.04
θ_m^2	45.97	16.32
θ_p	5.44	3.23

D_{33}°, the isotopic diffusion coefficient of tritiated water in pure water was obtained from reference (76).

TABLE 4.4

Counterion and Co-ion Self Diffusion Coefficients.

$\theta = D_{33}^{o} / D_{33}$

	C60N	C60E
D_{11} ($cm^2\ sec^{-1}$) x 10^7	3.62	7.47
$D_{11}\theta$ ($cm^2\ sec^{-1}$) x 10^6	1.58	2.41
$D_{11}\theta_m$ ($cm^2\ sec^{-1}$) x 10^6	2.45	3.02
$D_{11}\theta_p$ ($cm^2\ sec^{-1}$) x 10^6	1.97	2.41
D_{11}^{o} ($cm^2\ sec^{-1}$) x 10^6	5.10	5.90
D_{22} ($cm^2\ sec^{-1}$) x 10^6	2.64	3.70
$D_{22}\theta$ ($cm^2\ sec^{-1}$) x 10^5	1.15	1.20
$D_{22}\theta_m$ ($cm^2 sec^{-1}$) x 10^5	1.79	1.49
$D_{22}\theta_p$ ($cm^2 sec^{-1}$) x 10^5	1.43	1.20
D_{22}^{o} ($cm^2 sec^{-1}$) x 10^5	1.23	1.49

The D_{11}^{o} values obtained in equimolal $CaCl_2$ from reference (79).

both C60N and C60E membranes. The experimental values obtained were corrected for the effect of film diffusion at the membrane-solution interfaces. It was found (section 3.9) that this correction was significant only for counterion diffusion showing that co-ion and water diffusion through the unstirred films was unimportant as a rate-determining step (Appendix A.4). This method of correction is due to Scattergood and Lightfoot (34).

It is seen (tables 4.3, 4.4) that the coefficients for both membranes decrease in the order D_{33}, D_{22}, D_{11} as found in studies of aqueous calcium salts ($CaCl_2$) and this order was also found for the sodium form of these exchangers (44).

A comparison of normal and expanded forms cannot be made without consideration of tortuosity effects. The membranes contain different volume fractions of impermeable polymer and consequently in the expanded form which contains more water the tortuosity effect will be lower. Thus the expanded form would be expected to show higher values for corresponding D_{ii} values and this is illustrated in table 4.4. The tortuosity effect may however be estimated although, since the statistical values of diffusional pathways are not known in this system, all estimates must be considered approximate.

4.2.1 Tortuosity: Transport through a membrane occurs in continuous aqueous paths between polymer chains which are themselves impermeable. The AMF C60 membrane contains 35% styrene and about 65% polyethylene and tortuosity, in this case, involves circumventing the inert polymer polythene as well as the chains of polystyrene in the matrix. One consequence of this obstruction effect is that the diffusional path length through the membrane will be greater than the membrane thickness/

thickness (d). The measured diffusion coefficient of the exchanger will be lower than that in an analogous solution by a factor of θ and will be a function of the fractional "pore" volume V_w in the membrane phase.

Several estimates of θ have been calculated on the analogous dielectric situation (62) but these have been restricted to systems where the obstructing material was of small volume fraction and in the form of spherical particles. A more general treatment by Brown (63) is also restricted and is only applicable when each mobile species has similar permeability in the two phases.

Studies by Wheeler (64), Mackay and Meares (65) and Prager(66) have related the tortuosity factor to the volume fraction (V_w) of the pore liquid in the exchanger.

Wheeler's suggestion that,

$$\theta = \frac{2}{V_w} \qquad (4.3)$$

is however unsatisfactory because θ should tend to 1 as V_w tends to unity.

Mackay and Meares, on the basis of a lattice model, have calculated θ to be,

$$\theta = \left(\frac{2}{V_w} - 1 \right)^2 \qquad (4.4)$$

and this relationship has been widely tested. A good agreement is obtained between membrane diffusion coefficients of counterions, co-ions and water in Zeokarb 315 phenol sulphuric acid membranes and their corresponding values in aqueous solutions of the same concentration (67). Other authors however have found the agreement to be less satisfactory (30)(40)(68)(69)(70)(71).

It /

It has been found in this work as in previous studies (30)(31)(44) that a better correspondence between diffusion coefficients of exchangers and of the analogous electrolyte solutions is obtained when the tortuosity factor developed by Meares is reduced to,

$$\theta_m = \left(\frac{2}{V_w} - 1 \right) \qquad (4.5)$$

This factor θ_m used outwith the context of the original derivation must be considered to be empirical for these studies.

The application of a lattice model must lead to over-simplification, particularly in the assumption that all path lengths are equal. There will, in practice, be a distribution of path lengths in the exchanger and those which are shorter than average will make a disproportionately large contribution to the total flux thus causing overcorrection of the diffusion coefficients.

Prager (66) has derived an expression for θ, (θ_p), using a treatment which is purely theoretical and involves no knowledge of the membrane other than of the volume fractions of the permeable and impermeable regions. No estimated tortuosity correction can be made, however, which will be precise without a detailed statistical formulation of the membrane which is being studied. The Prager estimate has however been found to be useful in other studies relating exchanger diffusion to diffusion in free aqueous solutions of model electrolytes (72). The scaling factor θ can therefore only be regarded as approximate and, for practical purposes, comparison is made using θ_m and θ_p. The expression for θ_p is,

$$\theta_p = \frac{2}{V_w} - \frac{0.5\ (\ln V_w)^2}{(1 - V_w + V_w \ln V_w)} \qquad (4.6)$$

If V_w is close to unity only the first term $\frac{(2V_w - 1)}{(V_w + 1)}$ of the expansion of the series for $\ln V_w$ need be used. The equation now becomes/

becomes/

becomes,

$$\theta_p = \frac{2}{V_w} - \frac{2}{1 + V_w} \qquad (4.7)$$

which is in a form similar to eqn (4.5) since, as V_w tends to 1, θ_p tends to $(\frac{2}{V_w} - 1)$, which is designated θ_m in eqn (4.5).

Investigation of the relative applicability of the three equations (4.4)(4.5)(4.7) should, in theory, merely involve measuring D_{ii} (the diffusion coefficient of one species in the membrane) and D^o_{ii} (the diffusion coefficient of the same species in a solution of concentration equal to the internal concentration of the membrane). The ratio D^o_{ii} / D_{ii} may then be compared with calculated values for θ. There are, however, certain restrictions to such tests. A species must be selected which does not interact appreciably with the exchanger matrix and for this reason water diffusion coefficients would appear to be most useful. Ionic species are intrisically less useful since the counterions interact with the fixed charge on the matrix and the co-ions interact with counterions and unless these interactions are identical to those in the model solution , additional factors will influence the relative magnitudes of D^o_{ii} / D_{ii}. Liquid water is well structured and because its concentration is high inside the membrane all water-ion interactions are small compared with the water-water interaction. (This concept is discussed in Section 5.3).

It is noted at this point that species which have different paths for diffusion will have different tortuosities. If voids were to exist in the AMF C60 membrane the co-ion would be concentrated mainly in such spaces and might have more direct routes across the membrane. Studies of the sodium forms of such membranes (44) have shown that this is unlikely since D_{22}, D_{11} and D_{33} all tend to decrease with increasing concentration of external electrolyte. This being the case the C60 exchanger may be considered as relatively homogeneous in /

in which the isotopic diffusion characteristics are similar to volume diffusion in free aqueous electrolytes which also decreases with concentration (73)(74)(75). The effect of increased tortuosity as the membrane shrinks with increasing concentration of external electrolyte would enhance this effect.

4.2.2 Water Diffusion: The isotopic diffusion coefficient of water in the exchanger was determined using tritiated water as described in section 3.9. The results obtained are shown in table 4.3. The suggestion (section 4.2.1) that water in the membrane behaves in a manner similar to pure water may be investigated by evaluating the ratio D^{o}_{33}/D_{33} where D^{o}_{33} is the isotopic diffusion coefficient of tritiated water in pure water (76). It is seen (table 4.3) that eqn 4.4 (θ_m^2) greatly overestimates the experimental tortuosity value whereas the ratio D^{o}_{33}/D_{33} corresponds reasonably well with the θ values obtained from the simplified Meares equation (4.5) and from the Prager equation (4.7). Comparison with the θ_p value is particularly good (as it is for both C60N and C60E in the sodium form at external concentration 0.1M (77)).

The observation that pure water and the water in the exchanger appear to behave in a similar manner is interesting because the polyethylene and polystyrene of the matrix might well be expected to alter water structure within the exchanger pores. It appears therefore that the surface charge of sulphonate anions masks the polymer effect and confers upon the matrix the characteristics of a simple anion. Indeed n.m.r. studies on sulphonate exchangers indicate that water within such a material is structurally similar to bulk water solvent (78). Water diffusion data are therefore particularly suitable for/

for a test of tortuosity expressions.

4.2.3 Counterion and Co-ion Diffusion: The self-diffusion coefficients of the counterions and co-ions were obtained for both C60N and C60E membranes in an equilibrium solution of 0.05m $CaCl_2$. The experimental values were corrected for film diffusion in the previous chapter (section 3.9). As a result of the difficulties involved in measuring the co-ion uptake (section 3.8) the uncertainty in the values of the co-ion self-diffusion coefficients is much greater than the experimental accuracy of the diffusion flux measurements (which were reproducible to $\pm$ 2%). It should be noted, however, that this uncertainty in co-ion uptake (c_2) does not affect the magnitude or accuracy of the phenomenological coefficients obtained directly from the co-ion self-diffusion coefficient values because,

$$D_{ii} = \frac{RT}{c_i (R_{ii} - R_{ii'})} \qquad (2.55)$$

and since eqn. 2.55 shows c_i to be in the denominator of the expression for D_{ii}, $(R_{ii} - R_{ii'})$ values do not depend on c_i.

The self-diffusion coefficients obtained were shown in table 4.4. As expected, the coefficient values are greater in the C60E membrane which has a higher water content and a more open structure.

Comparison of the counterion and the co-ion self-diffusion coefficients reveals that the co-ion (chloride) mobility is much greater than that of the calcium counterion and this order, as stated above, is also observed for the diffusion coefficients of calcium and chloride in aqueous calcium chloride (79). The chloride ion, as in aqueous solution, is intrinsically more mobile than the calcium cation. Wyllie (80) has however proposed that a large difference in /

in the ion mobilities in the exchanger could be partly explained by assuming that the species with the greater affinity for the fixed sites in the membrane will be further retarded by interaction with those sites. For most exchangers of the sulphonate type counterion diffusion is typically a rising function with increasing external concentrations while co-ion coefficients typically decrease (65)(81)(82)(83)(84).

Spiegler (85) has suggested that such behaviour would be expected of an exchanger which contained near continuous void regions. At lower electrolyte penetration, counterions would be concentrated in regions of high fixed-charge and cross-linking and a low counterion diffusion coefficient would be expected. Additional counterions of invading electrolyte (which would occupy the void regions preferentially) would consequently have a higher mobility and would increase the overall rate of diffusion. As discussed above, the C60 exchangers in their sodium form (44) show no such effects and may be considered as relatively homogeneous in which the isotopic diffusion characteristics are similar to volume diffusion in free aqueous electrolytes which also decrease with concentration (73)(74)(75). The effect of increased tortuosity as the membrane shrinks would enhance this effect.

It may therefore be concluded that the relative magnitudes of the isotopic diffusion coefficients of the calcium and chloride ions in the C60 membrane is a reflection of their relative mobility in aqueous solution.

The values of D_{22} are similar to those for chloride in equimolal calcium chloride (D^{o}_{22}) (table 4.4) but although, as in the solution analogue, calcium ions would be expected to be less mobile than chloride, $D_{11}\theta$ is, by any estimate of θ, some 50% of the value for

aqueous/

aqueous calcium chloride. This effect may be due to ion-association as in Wyllie's theory discussed above, but in section 5.4 the isotopic diffusion coefficients are subdivided into the relative contributions of the frictional interactions between the ion and its environment in the membrane and of Ca^{2+}- Ca^{2+} isotopic friction. The environmental contributions are similar to those in aqueous calcium chloride (section 6.6) but the isotopic friction is anomalously high.

4.3 Electro-osmosis: Electro-osmosis experiments were performed as described in section 3.14. The water transference number t_3, which is the number of moles of water transferred when one Faraday of electricity passes, was obtained for both C60N and C60E membranes in their calcium forms. The transference number is defined by eqn 2.31,

$$t_3 = \frac{J_3 F}{I} \qquad (2.31)$$

where J_3 is the flux of water (mol cm^{-2} s^{-1}), F is the Faraday and I is the current density (A cm^{-2}).

An accurate determination of the t_3 values must involve an investigation of the volume changes which occur in each half-cell as a result of the passage of calcium ions through the membrane and of the chemical reactions at the silver-silver chloride electrodes. As one Faraday of electricity passes through the membrane, t_+ equivalents of calcium is transferred into the cathode chamber and t_- equivalents of chloride to the anode. At the cathode silver chloride is reduced to silver. The apparent water transference number $t_3(app)$ is therefore related to the true t_3 value by the equation,

$$t_3(app) = t_3 + \frac{t_1 \bar{V}_{CaCl_2} + \bar{V}_{Ag} - \bar{V}_{AgCl}}{\bar{V}_3^o} = t_3 + \beta$$

$\bar{V}_i$/

TABLE 4.5

Transport properties of A.M.F. -60 membranes.

External concentration 0.05m $CaCl_2$

	C60N	C60E
Specific Conductivity (K)($ohm^{-1}cm^{-1}$) $x10^2$	0.521	1.10
t_2 (transport number of co-ion)	0.011	0.018
t_3 (transference number of water)	8.97	10.30

$\bar{V}_i$ is the partial molal volume of species i and β is the correction factor. The partial molal volumes are derived and evaluated as described in appendix A.6.

The corrected t_3 values for the C60N and C60E membranes are 8.97 and 10.30 respectively (table 4.5) were much closer than was expected from transport data obtained both from this work and from studies on the sodium form of similar membranes (43). For example, osmotic flow experiments (section 3.13) show that the ratio of water flux through the C60E membrane to water flux through the C60N membrane is 2.3 to 1 (table 4.6). This compares with a ratio for the membranes in the sodium form of 2.5 to 1. The t_3 values for the equivalent sodium form are 10.75 and 15.77 for C60N and C60E respectively. It is noted also that the ratio $\frac{Z_1 t_3}{t_1}$ drawn as a function of $\frac{c_3}{c_1}$ is not linear through the origin as observed in other studies (44). The implications of this observation are discussed in sections6.5 and 6.7.

"Salt Model" calculations (section 6.7) have been used to predict t_3 values for the sodium form of the C60 membranes to within 10% (table 6.5). Insufficient calcium chloride solution data is available at concentrations in excess of 1.0 molar to predict t_3 values for the calcium form of C60N (which has an internal molality of 1,70). It can be seen however from the calculation outlined in section 6.6 that, while the observed t_3 value for the C60E (internal molality 1.07 in the calcium form) is greatly overestimated (19.9), by far the most variable parameter is the water concentration c_3. On this basis the transference number for the C60N would therefore be smaller relative to t_3 for C60E than is observed.

A factor which contributes to the results obtained is the much greater/

greater co-ion uptake of the expanded membrane (table 4.1). As will be discussed in the following section, the water transference number, t_3, may be expressed as,

$$t_3 = \frac{Z_1 l_{13} + Z_2 l_{23}}{\alpha} \qquad (2.32)$$

where Z_1 and Z_2 are the valencies of the counterion and co-ion respectively, l_{13} and l_{23} are the mobility coefficients concerned with the interaction of water with counterion and co-ion respectively.

$$\alpha = Z_1^2 l_{11} + 2Z_1 Z_2 l_{12} + Z_2^2 l_{22} \qquad (2.28)$$

where l_{11} and l_{22} are the direct mobility coefficients of the counterion and co-ion and l_{12} is the corresponding cross-coefficient.

It will be seen (table 5.1) that l_{23} and l_{13} are both positive in this system. $Z_2 l_{23}$ will therefore be negative. l_{23} is a measure of the interaction between co-ion and water and so, as the co-ion concentration increases, $Z_2 l_{23}$ will have an increased effect in reducing t_3. This contribution has to be small however since the co-ion concentration c_2 is only 1% of c_1 and it is not proposed as the sole reason for the unexpectedly low t_3 value in the C60E membrane.

It was noted that the t_3 values obtained did not vary with current density within the range 1 - 4 mA cm^{-2}. This is however not a general phenomenon and some authors have found that at external solution concentrations of 0.1 molar or less, $Z_1 t_3$ increases with decreasing current density. (This topic has been well reviewed in reference 55).

4.4 Conductivity: The specific conductivities of both C60N and C60E membranes were measured as described in section 3.10 and are tabulated (table 4.5). The specific conductivity of an electrolyte solution at

a/

a given concentration is governed by the mobility of the ions and this mobility depends on the concentration and nature of these ions. A second factor, tortuosity, must be taken into account, however, when considering transport processes in a membrane phase. The degree of tortuosity of the membrane has a direct bearing on the observed mobility of the ions within it. Reference to Table 4.5 shows that the tortuosity factor is of primary importance. Although the expanded membrane C60E contains a lower concentration of mobile ions than the normal C60N (Table 4.1) the specific conductivity of the C60E and C60N are 1.10×10^{-2} and 0.52×10^{-2} ohm^{-1} cm^{-1} respectively.

Comparisons may be made between the experimentally observed specific conductivity values and these calculated using the Nernst-Planck theory (section 2.52). The applicability of this theory to the system under investigation is discussed in terms of those and similar comparisons in section 5.5.

4.5 Transport Numbers: The co-ion transport number t_2 was found experimentally for both C60N and C60E membranes. The t_2 values were 0.011 and 0.018 for the C60N and C60E membranes respectively. The higher t_2 value for the expanded form reflects the higher concentration of co-ion in the membrane while the counterion concentration (c_1) is slightly lower (Table 4.1).

These t_2 values are far larger than the values of 0.002 and 0.005 obtained for similar membranes (C60N and C60E respectively) in the sodium form. (43). This is largely a result of the higher co-ion concentration in both calcium forms (c_2 is 3.14×10^{-3} and 6.83×10^{-3} mmol ml^{-1} for the calcium form and 2.40×10^{-3} and 5.20×10^{-3} mmol ml^{-1} for the sodium form of the C60N and C60E membranes respectively). The relative mobilities of the counterions however must /

TABLE 4.6

Salt and Osmotic Flows

Membrane	C60N	C60E
Concentration gradient	0.0248m/0.0764m	0.0242m/0.0733m
$\left\{-\frac{du_{12}}{dx}\right\}_{x10^{-5}}$ (joules mole^{-1}cm^{-1})	2.488	2.245
$\left\{-\frac{du_3}{dx}\right\}$ (joules mole^{-1}cm^{-1})	-205.43	-179.1
J_s (moles cm^{-2} sec^{-1}) x 10^{10}	3.686	9.710
J_3 (moles cm^{-2} sec^{-1}) x 10^{8}	-4.981	-11.484

must also be considered. The calcium ion is intrinsically less mobile than the sodium ion in an equinormal solution (22)(79)(86). This would also appear to be the case in the membrane system since, for example, the self diffusion coefficient (corrected for path tortuosity and film diffusion) of the calcium counterion is much lower than that of the sodium. ($D_{Ca}\,\theta_m$ and $D_{Na}\,\theta_m$ are 3.02×10^{-6} and 7.80×10^{-6} cm^2 sec^{-1} respectively in the C60E membrane).

4.6 Salt and Osmotic Flows: A concentration gradient was set up across the membrane as described in section (3.13) by placing it between two solutions of approximately 0.025 molal and 0.075 molal calcium chloride (table 4.6). In such isobaric isothermal systems two chemical potential gradients (thermodynamic forces) are set up which act in opposite directions. The gradients are the result of differences in the chemical potentials of the salt and of the water on either side of the membrane. They are assumed for the purposes of this work to be linear across the membrane and are derived in section 2.4.1.2. The chemical potential gradient of the salt is designated by X_{12} and that of water X_3.

The salt gradient X_{12} may be evaluated by considering the relationship (equation 2.39),

$$\mu_{12} = r_1\mu_1 + r_2\mu_2 \qquad (2.39)$$

which for $CaCl_2$ becomes $\mu_{12} = \mu_1 + 2\mu_2 \cdot \mu_{12}$, μ_1 and μ_2 are the chemical potentials of the salt, 12, cation 1, and anion 2, respectively. r_1 and r_2 are the stoichiometric coefficients of the cation and anion respectively.

Since $\mu_i = \mu_i^o + RT \ln a_i$ under these conditions (where μ_i^o is the standard chemical potential of species i, R and T are the gas constant and absolute temperature and a_i is the activity of species i)

u_{12} /

μ_{12} now becomes

$$\mu_{12} = \mu_1^o + RT \ln a_1 + 2\mu_2^o + RT \ln a_2^2$$
$$= (\mu_1^o + 2\mu_2^o) + RT \ln a_1 a_2^2$$
$$\text{i.e. } \mu_{12} = \mu_{12}^o + RT \ln a_1 a_2^2 \qquad (4.8)$$

The mean molal activity coefficient γ_{12} of a salt may be expressed as

$$(\gamma_{12})^r = (\gamma_1)^{r_1} \cdot (\gamma_2)^{r_2} \qquad (4.9)$$

where γ_1 and γ_2 are the activity coefficients of cation and anion respectively, while $r_1 + r_2 = r$.

The molality of the salt m_{12} is expressed as

$$m_{12} = \frac{m_1}{r_1} = \frac{m_2}{r_2} \qquad (4.10)$$

where m_1 and m_2 are the cation and anion molalities.

Equation 4.8 now becomes for $CaCl_2$,

$$\mu_{12} = \mu_{12}^o + RT \ln (4m_{12}^3)\gamma_{12}^3$$
$$= \mu_{12}^o + 3RT \ln (\sqrt[3]{4}\, m_{12}\gamma_{12}) \qquad (4.11)$$

If a membrane of thickness d cm separates two solutions represented by indices ' and ".

$$X_{12} = \frac{\Delta\mu_{12}}{d} = \frac{3RT}{d} \cdot \ln \left\{ \frac{m'_{12}\gamma'_{12}}{m''_{12}\gamma''_{12}} \right\}$$

$$= \frac{3RT}{d}\, 2.3026 \left\{ \log \left\{ \frac{m'_{12}}{m''_{12}} \right\} + \log \gamma'_{12} - \log \gamma''_{12} \right\} \qquad (4.12)$$

Mean molal activity coefficients were obtained from Harned and Owen (87) and Robinson and Stokes (88).

The chemical potential gradient of water X_3 ($\frac{\Delta\mu_3}{d}$) may be evaluated /

evaluated by a similar approach since

$$X_3 = \frac{\Delta\mu_3}{d} = RT\,(\ln a_3' - a_3'') \qquad (4.13)$$

where a_3 is the water activity. This gradient has been derived in section 2.42, and equation 2.44 may be applied here where the pressure difference across the membrane is zero.

The measured salt and water fluxes J_s and J_3 are tabulated along with their corresponding forces (table 4.6). They are calculated using the equations 2.41 and 2.44

$$J_3 = \frac{1}{r_1}\left(l_{13} - \frac{t_1}{z_1}\alpha t_3\right)\left(- \frac{d\mu_{12}}{dx}\right) + \left(l_{33} - t_3^2\alpha\right)\left(- \frac{d\mu_3}{dx}\right) \qquad (2.41)$$

$$J_s = \frac{-z_1z_2}{r_1r_2}\left(\frac{l_{11}l_{22} - l_{12}^2}{\alpha}\right)\left(- \frac{d\mu_{12}}{dx}\right) + \frac{1}{r_1}\left(l_{13} - \frac{t_1t_3\alpha}{z_1}\right)\left(-\frac{d\mu_3}{dx}\right) \qquad (2.44)$$

It is to be noted that X_{12} and X_3 are opposite in sign as are the fluxes J_s and J_3. Further evidence for the more open structure of the C60E membrane exists since salt and water flow are about 2.5 times faster for this membrane although the corresponding forces are slightly smaller. The higher concentration of co-ion in the C60E (table 4.1) (section 4.1.2) and lower tortuosity allows a greater osmotic flow in the membrane.

Table 4.7

Measured water flow J_3 and product solution concentration c_p under hyperfiltration conditions at 25°C.

Concentration of the feed solution 0.05 molal.

Membrane	Measured J_3 (moles $cm^{-2} sec^{-1}$)	c_p (molal)
C60N	1.18×10^{-6}	0.0306
C60E	1.60×10^{-6}	0.0284

4.7 Hyperfiltration: Hyperfiltration studies were made as described in section 3.15. The concentration of the product solution and the rate of flow of water through the membrane are noted (table 4.7).

Salt flow, J_s, and water flow, J_3, were calculated using equations 2.45a and 2.45b,

$$J_s = L^1_{ss} X_s + L^1_{s3} X_3 \qquad (2.45a)$$

$$J_3 = L^1_{3s} X_s + L^1_{33} X_3 \qquad (2.45b)$$

X_s is the thermodynamic force produced by the electrolyte activity difference across the membrane. X_3 is evaluated using equation 2.47,

$$X_3 = \frac{P - P^o}{d} - \frac{r\,RTw_a}{d10^3}\left\{\phi_f m_f - \phi_p m_p\right\} \qquad (2.47)$$

where $P - P^o$ is the difference between applied pressure and standard state pressure. (1 atm. at 25°C).

In view of the inaccuracies in the hyperfiltration experiments, equations 2.45a and 2.45b were not used to complete the thermodynamic scheme and provide a sixth parameter. The results were used instead on a comparative basis to assess in direct terms the validity of the assumptions discussed in chapter 5.

CHAPTER 5.

Application of Transport Theories

In Chapter 2 it was shown that the properties of an ion-exchange membrane containing two ionic species and water are defined by six phenomenological transport coefficients. Under isothermal, isobaric conditions only five independent equations may be formulated and so certain assumptions regarding the magnitude of one minor coefficient are necessary. In the present series the sixth independent experiment was performed using pressure gradients as additional thermodynamic forces. The resultant fluxes of salt and water through the membranes were measured. The precision of these studies was, however, low ($\pm$ 5%) and of insufficient accuracy to allow that data to be incorporated in the solution of the general problem. (Subsequent to termination of this research other workers (41) have continued these pressure / desalination studies under more carefully controlled conditions and to much greater accuracy. It is hoped that in the final publication of these studies the complete set of six transport equations will be used). For present purposes a series of approximations to minor coefficients will be applied and the resulting solutions tested against pressure-study results, bearing in mind the lower precision in the latter.

5.1 Limiting Assumptions

5.1.1 Approximations for mobility coefficient calculations: Several approximations have been made to solve the five phenomenological equations (2.30a)(2.30b)(2.32)(2.41)(2.44) and these are based partly on experience gained from solution data (22)(89) and partly on the concentration dependence of the mobility coefficients.(43).

The simplest assumption is that the membranes are basically simple binary electrolytes of calcium (1) and membrane-bound sulphonate /

sulphonate (4)and that the co-ion concentration is small enough to be neglected. This approximation would seem to be reasonable since the molar co-ion concentrations c_2 are 0.718% and 1.60% of the counterion concentrations for the C60N and C60E membranes respectively and the corresponding values of the transport numbers for t he calcium counterion are 0.989 and 0.982. It is noted that the concentration data of the sodium form of the AMF C60 membranes (43) infer that that form is more suited to these approximations (the corresponding values of the ion concentration ratios are 0.245% and 0.541%). In the binary situation the phenomenological equations (2.18) simplify to,

$$J_1 = l_{11}X_1 + l_{13}X_3 \qquad (5.1a)$$

$$J_3 = l_{31}X_1 + l_{33}X_3 \qquad (5.1b)$$

and all coefficients involving co-ion,2, are neglected.

Since the co-ion is a minor component it may be assumed that the coupling coefficient l_{12} between counterion and co-ion is small compared with the direct coefficient l_{11} for the counterion.

Examination of equation 2.30a reveals,

$$t_1 = \frac{z_1^2 l_{11} + z_1 z_2 l_{12}}{\alpha} \qquad (2.30a)$$

that for calcium chloride (where $Z_1 = 2$ and $Z_2 = -1$) the effect on l_{11} of approximating l_{12} to zero would appear to be reduced still further. The approximation ($l_{12} = 0$) is however less good with regard to the direct mobility of the co-ion l_{22}. It is possible that l_{12} may be a significant fraction of l_{22} which is the smallest of the direct coefficients and, if this were so, the approximation $l_{12} = 0$ would seriously underestimate l_{22}; eqn 2.30b,

$$t_2 = \frac{z_2^2 l_{22} + z_1 z_2 l_{12}}{\alpha} \qquad (2.30b)$$

When/

Table 5.1

Mobility Coefficients

External Solution 0.05m $CaCl_2$

	Assumption	$l_{11}\times10^{13}$	$l_{12}\times10^{16}$	$l_{22}\times10^{15}$	$l_{13}\times10^{12}$	$l_{23}\times10^{14}$	$l_{33}\times10^{10}$
C60N	Binary	1.399			2.510		2.875
	$l_{12}=0$	1.384		6.156	2.531	4.276	3.468
	$l_{23}=0$	1.383	-0.420	6.072	2.510		3.210
	$R_{23}=0$	1.383	-1.143	5.927	2.510	0.2074	3.205
C60E	Binary	2.948			6.072		7.663
	$l_{12}=0$	2.894		21.22	7.071	199.7	21.55
	$l_{23}=0$	2.887	-15.9	18.04	6.072		9.033
	$R_{23}=0$	2.883	-16.23	17.98	6.055	-3.408	8.822

Units for l_{ik} are $mole^2\ J^{-1}\ cm^{-1}\ s^{-1}$.

When calcium chloride is the electrolyte under consideration the effect of the approximation $l_{12} = 0$ on l_{22} seems to be enhanced by the valency terms. t_2, although small, is positive and so there is no doubt that l_{22} exceeds l_{12}. Inspection of the appropriate phenomenological equations will show that this approximation underestimates all other mobility coefficients to a degree.

Cross-coefficient l_{23} is a measure of the coupling between co-ion, 2, and water, 3, and may be evaluated using equations 2.32 and 2.44 and the approximation $l_{12} = 0$. Results (table 5.1) show that l_{23} is large compared with l_{22} but is smaller than l_{13}, the counterion-to-water coupling coefficient.

In equation 2.32,

$$t_3 = \frac{Z_1 l_{13} + Z_2 l_{23}}{\alpha} \qquad (2.32)$$

the valency terms appear to make the neglect of l_{23} an even better assumption relative to the $l_{12} = 0$ approximation for the case of a 2:1 electrolyte (e.g. $CaCl_2$) than for the study of a 1:1 electrolyte such as sodium chloride in which it has been used with some success. Since the concentration percentage of co-ion to counterion is low for both membranes (0.718% and 1.60% for C60N and C60E respectively) one would expect that the presence of co-ion would not affect significantly the amount of water transferred by the electric current and would not influence t_3 by an amount commensurate with the experimental uncertainty in evaluating this parameter ($\pm 2\%$). It will in fact be shown (table 5.1) that in all cases except the $l_{12} = 0$ approximation for the C60E membrane neglect of l_{23} in equation 2.32 causes a variation of l_{13} which is smaller than the effect of the experimental error involved in evaluating t_3 (section 3.14).

When/

TABLE 5.2

Frictional Coefficients

$0.05mCaCl_2$ external solution at 25°C.

C60N Membrane

	a	b	c	d	
	$l_{12}=0$ +matrix inversion	$l_{23}=0$ +matrix inversion	$R_{23}=0$	$R_{22'}=0$	binary
R_{11} x10-12	8.342	8.424	8.427	7.734	8.475
R_{12} x10-11	4.233	0.583	1.395	32.27	
R_{13} x10-10	-6.094	-6.588	-6.596	-2.394	-7.400
R_{22} x10-14	1.626	1.647	1.687	1.497	
R_{23} x10-10	-2.314	-0.0456		19.36	
R_{33} x10-9	3.331	3.631	3.636	1.083	4.124
R_{14} x10-12	-3.189	-3.147	-3.148	-3.500	-3.025
R_{24} x10-11	-4.192	-6.153	-6.781	10.13	
R_{34} x10-10	-2.393	-2.645	-2.650	-5.032	-3.059
R_{44} x10-11	19.94	20.151	20.16	1.835	20.14
$R_{11'}$ x10-12	-7.318	-7.236	-7.233	-7.926	
$R_{22'}$ x10-14	0.129	0.150	0.190		

Units for R_{ik} are J cm s $mole^{-2}$.

TABLE 5.2 (cont.)

Frictional Coefficients

$0.05mCaCl_2$

C60E Membrane

	a	b	c	d	
	$l_{12}=0$ +matrix inversion	$l_{23}=0$ +matrix inversion	$R_{23}=0$	$R_{22'}=0$	binary
R_{11} x10-12	3.788	4.037	4.054	3.571	4.055
R_{12} x10-11	12.82	3.558	3.132	20.98	
R_{13} x10-10	-1.361	-2.714	-2.781	-0.1710	-3.213
R_{22} x10-14	0.5206	0.5546	0.5565	0.4905	
R_{23} x10-10	-5.246	-0.2392		-9.655	
R_{33} x10-9	0.5573	1.289	1.324	-0.873	1.560
R_{14} x10 12	-1.564	-1.330	-1.320	-1.772	-1.189
R_{24} x10-11	3.028	-5.647	-6.072	10.66	
R_{34} x10-10	-0.726	-1.996	-2.055	-2.443	-2.464
R_{44} x10-11	9.754	11.96	12.07	26.44	12.38
$R_{11'}$ x10-13	-3.992	-3.743	-3.726	-4.209	
$R_{22'}$ x10-14	0.0301	0.0641	0.0660		

Units for R_{ik} are J cm s mole $^{-2}$.

When either of the approximations $l_{12} = 0$ and $l_{23} = 0$ is made the remaining coefficients alter slightly to compensate. This imbalance becomes more evident when the mobility coefficient matrix is inverted to obtain R-coefficients which relate to "mole to mole" friction.

5.12 Frictional or R -Coefficient Assumptions: The R -coefficients in table 5.2 were calculated using four separate assumptions. Sets (a) and (b) were calculated by matrix inversion of the corresponding sets of l-coefficients (table 5.1). A third approximation, $R_{23} = 0$, (c), was originally proposed by Staverman (90) on the assumption that if the co-ion uptake is low the co-ion-dipole friction would be small enough to be neglected. Although assumption (c) would appear to be intrinsically unsatisfactory because R-coefficients measure friction on a mole-to-mole basis, table 5.2 shows that it yields results which are in good agreement with sets (a) and (b). It may also be noted from table 5.2 that R_{23} has a magnitude comparable with several R-coefficients. Consideration of the term $-c_2R_{23}$, which is a measure of the coefficient of friction between one mole of water and those co-ions per unit volume of the exchanger (table 5.4), shows that it is negligibly small compared to the interactions of one mole of water with other ions.

Inspection of the phenomenological equations (2.48a, 2.48b, 2.48c, 2.50a, 2.50b) shows that in each equation the term containing the frictional coefficient, R_{23}, is at least an order of magnitude smaller than any other (table 5.2). This condition has been fulfilled in earlier studies of the sodium form of the C60 system (43).

A fourth group of coefficients (d) was obtained from the co-ion self-diffusion results using the approximation $R_{22} = 0$ which was made by/

by Spiegler in his earliest analysis discussed in section 2.4.5. The term $c_i R_{ii'}$, measures the frictional interaction between one mole of tracer isotope i' with those bulk isotopes, i, per unit volume of exchanger, while $c_i R_{ii}$ measures the sum of the frictional effects between one mole of i and all other species per unit volume. Since the co-ion is a minor component of the exchanger, $c_2 R_{22'}$ is small compared with $c_2 R_{22}$ which involves frictional interactions with all major components 1,3 and 4, and so the assumption would appear to be reasonable in this situation. (Supporting evidence for these arguments may be found by referring to the "Salt Model Calculations" of chapter 6).

It has been illustrated as discussed above (section 4.12) that co-ion concentrations in the calcium form of the C60 membranes are higher than in the sodium form provided the equilibrium solutions are equinormal (0.1N) and it is not suggested that the approximations described above can be more valid than in the sodium form. Indeed it will be shown (table 5.1) (43) that these assumptions produce less consistent results for the calcium form.

It is of interest, however, to compare directly the individual mobility and frictional coefficients of the sodium and calcium forms of the C60 system.

In order to determine the relationship which would be expected from such a comparison a general correlation of these coefficients may be made for a membrane or solution in which one ionic species is univalent and divalent. For this purpose we shall consider a hypothetical salt A^+Cl^- at concentration c_a and normality N. We shall now suppose that there exists a 2:1 salt with a divalent cation $B^{2+}(Cl^-)_2$ which has identical thermodynamic and transport properties to ACl at

equal/

equal normality N. An obvious concentration relationship exists ($c_a/_2 = c_b$) and since transport properties are defined equal it will be generally true that,

$$J_a = 2J_b \text{ and } u_{ACl} = \frac{1}{2} u_{BCl_2}$$

Consequently,

$$X_a = \frac{1}{2} X_b.$$

Co-ion flows and forces would be unaffected. For such an idealised pair of electrolytes the phenomenological equations would be,

$$J_a = L_{aa}X_a + L_{a2}X_2 + L_{a3}X_3$$

$$J_2^a = L_{2a}X_a + L_{22}X_2 + L_{23}X_3$$

$$J_3 = L_{3a}X_a + L_{32}X_2 + L_{33}X_3$$

for the salt A^+Cl^- and,

$$J_b = l_{bb}X_b + l_{b2}X_2 + l_{b3}X_3$$

$$J_2^b = l_{2b}X_b + l_{22}X_2 + l_{23}X_3$$

$$J_3 = l_{3b}X_b + l_{32}X_2 + l_{33}X_3$$

for the salt $B^{2+}(Cl^-)_2$.

It is easily shown that,

$$l_{bb} = \frac{L_{aa}}{4}\ ;\ l_{b2} = \frac{L_{a2}}{2} = l_{2b};\ l_{b3} = \frac{L_{a3}}{2}\ ;$$

$$l_{23} = L_{23};\ l_{33} = L_{33};\ l_{22} = L_{22}.$$

Inversion of the mobility coefficient matrices would yield the following identities where R is the frictional coefficient for the salt $B^{2+}(Cl^-)_2$, and $\underset{\sim}{R}$ is the frictional coefficient for A^+Cl^-,

$$R_{bb} = 4\underset{\sim}{R}_{aa} \qquad R_{b4} = 2\underset{\sim}{R}_{a4}$$

$R_{b2}/$

Table 5.3

Comparison of aqueous solution transport coefficients for Equinormal NaCl and $CaCl_2$ (2.0N) at 25°C.

Solution	NaCl	$CaCl_2$	$\frac{Na}{Ca}$	Observed	Predicted
$l_{11}x10^{12}$	7.62	1.42	$\frac{L_{11}}{l_{11}}$	5.36	4.0
$l_{12}x10^{12}$	1.82	1.15	$\frac{L_{12}}{l_{12}}$	1.58	2.0
$l_{22}x10^{12}$	12.07	11.99	$\frac{L_{22}}{l_{22}}$	1.006	1.0
$R_{11}x10^{-11}$	1.36	7.62	$\frac{R_{11}}{R_{11}}$	0.16	0.25
$R_{22}x10^{-11}$	0.860	0.904	$\frac{R_{22}}{R_{22}}$	0.952	1.00
$R_{12}x10^{-10}$	2.06	-7.32	$\frac{R_{12}}{R_{12}}$	0.28	0.50
$R_{13}x10^{-9}$	-4.34	-8.74	$\frac{R_{13}}{R_{13}}$	0.496	0.500
$R_{23}x10^{-9}$	-2.46	-1.78	$\frac{R_{23}}{R_{23}}$	1.38	1.00
$R_{33}x10^{-7}$	25.55	22.49	$\frac{R_{33}}{R_{33}}$	1.33	1.00

The primary transport data for aqueous $CaCl_2$ solution was obtained from reference (79) and processed (appendix A.8). The transport coefficients pertaining to 2.0N aqueous NaCl were obtained from reference (22).

Such a comparison will be referred to in the text as an Equivalent Valency Model.

$R_{b2} = 2R_{a2}$ $\quad R_{22} = R_{22}$ $\quad R_{34} = R_{34}$

$R_{b3} = 2R_{a3}$ $\quad R_{24} = R_{24}$ $\quad R_{44} = R_{44}$

$R_{23} = R_{23}$ $\quad R_{33} = R_{33}$

The mobility and frictional coefficients of 1:1 and 2:1 salts may be compared by means of the above identities although the individuality of each electrolyte must make the above but useful guides to relative magnitudes. It is immediately obvious, however from these identities that the valency effects on the limiting assumptions discussed above (equations 2.30 and 2.32) are illusory and on this basis assumptions $l_{12}=0$ and $l_{23}=0$ are probably equally valid.

The sodium form of the C60 system has been extensively investigated (30)(43)(44)(91) and it has been ascertained that the frictional and coupling interactions are similar in the membrane to those of sodium chloride in solution when allowance has been made for tortuosity and concentration corrections. The hypothetical 2:1 salt $B^{2+}(Cl^-)_2$ corresponding to sodium chloride must show equal similarities. The individual coupling and frictional interactions of the calcium and sodium forms of the membrane system may therefore be compared in the context of this hypothetical situation.It is useful, however,initially to compare the transport properties of equinormal aqueous solutions of sodium chloride and calcium chloride in order to determine the predictive qualities of the model $B^{2+}(Cl^-)_2$electrolyte in the simpler solution system.

Reference to table 5.3 in which the mobility and frictional coefficients of sodium chloride and calcium chloride in equinormal solutions (2.0N) are compared shows that l_{11} for the calcium ion is lower than the model $B^{2+}(Cl^-)_2$ suggests. The direct mobility coefficient ratio L_{22}/l_{22} does, on the other hand, show extremely good agreement with the predicted value. The frictional coefficient ratio/

ratio R_{13}/R_{13} is estimated remarkably well by the model. Other frictional interactions directly involving the calcium ion R_{11} and R_{12} are underestimated while the water-co-ion R_{23} and water-water R_{33} values are overestimated. It is noted however that all coefficients are predicted to within $\pm$ 40% for major coefficients. This comparison, although only semi-quantitative, provides a basis for expectations on the correlation of calcium and sodium forms in the membrane which are, by virtue of their matrix-fixed sulphonate charge, effectively equi-normal systems.

5.2 Results: The results of the calculations using the assumptions described are given in tables 5.1 and 5.2 as l_{ik} and R_{ik} coefficients respectively.

Table 5.1 contains the l_{ik} coefficients obtained by applying the approximations $l_{12}= 0$ and $l_{23}= 0$ as well as those derived from matrix inversion of the R- coefficients calculated by assuming $R_{23}= 0$. The applicability of these assumptions appears to decrease in the order $l_{23}= 0$, $R_{23}= 0$, $l_{12}= 0$. It is noted that although l_{12} is found to be negative its value is so low as to be insignificant compared with l_{22} which is the next smallest mobility coefficient.

The approximation $R_{22'} = 0$ was found to yield R-coefficients which do not agree well with those obtained using the other approximations (table 5.2). It was therefore decided against including the l-coefficients obtained using this assumption ($R_{22'} = 0$) in the overall thermodynamic scheme.

5.3 Discussion:

5.3.1 Mobility l_{ik} - Coefficient Values:

5.3.1 Mobility l_{ik}- Coefficient Values: Although the mobility coefficients calculated using the $l_{12} = 0$ approximation (table 5.1) and their corresponding R-coefficients (table 5.2) compare closely with these obtained using the approximations $l_{23} = 0$ and $R_{23} = 0$, this comparison is less good than in the sodium form of the membranes.

The coupling coefficient l_{23} is particularly sensitive to experimental uncertainties since it is calculated from the difference of two almost equal quantities (eqn 2.32). The wide variation observed in its values (table 5.1) is therefore rationalised and, as seen, it remains a very small influence on the water transference number.

Examination of table 5.1 will show that the direct coefficient l_{33} varies more than any other with the differing approximations. l_{33} is evaluated using equation 2.41 and a calculated value of l_{13}. As discussed above, this value of l_{13} varies according to the approximation applied. When $l_{12} = 0$, l_{11} and l_{22} are minima and l_{13} is underestimated. If however $l_{23} = 0$, l_{13} has a minimum value. The variation in l_{13} is emphasised in equation 2.41.

$$J_3 = \frac{1}{r_1}\left(l_{13} - \frac{t_1}{Z_1}\alpha t_3 \right)\left(- \frac{d\mu_{12}}{dx} \right) + \left(l_{33} - t_3^2\alpha \right)\left(- \frac{d\mu_3}{dx} \right) \quad (2.41)$$

by its association with the predominant force X_{12} under the conditions stated (table 4.6) and this is reflected in the l_{33} values quoted. Consistently accurate hyperfiltration results would go far to providing a precise estimation of $(l_{33} - t_3^2\alpha)$ and as discussed above such studies are at the moment being investigated (41).

It may be concluded that neglect of co-ion coupling is less

useful/

Table 5.4

External solution 0.05m $CaCl_2$ at 25°C

membrane	C60N	C60E
J_s (observed) (moles $cm^{-2} sec^{-1}$) $\times 10^{10}$	3.686	9.710
J_s (calculated) (moles $cm^{-2} sec^{-1}$) $\times 10^{10}$	3.8	11.7

Comparison of observed salt flows J_s for the normal and expanded C60 membranes in 0.05m $CaCl_2$ at 25°C with those J_s values calculated using equation 5.2.

useful in the calcium form than in the sodium form of both C60N and C60E membranes and this may be attributed to the increased co-ion uptake.

It is however worthy of note that the expression for the salt flow, J_s, (equation 5.2) which is a rearrangement of equation 2.44 with $l_{12} = l_{23} = 0$,

$$J_s = \frac{\alpha t_2}{z_1} \left\{ -\frac{t_1}{r_1 r_2 z_2} \left\{ -\frac{d\mu_{12}}{dx} \right\} + \frac{t_3}{r_1} \left\{ -\frac{d\mu_3}{dx} \right\} \right\} \qquad (5.2)$$

shows that J_s is controlled primarily by the transport number of the co-ion in the membrane.

The salt flows calculated using equation (5.2) were compared with the experimentally observed values (table 4.6). As seen in table 5.4 observed and calculated values for the C60N were 3.7×10^{-10} and 3.8×10^{-10} mol cm^{-2} sec^{-1}, and 9.7×10^{-10} and 11.7×10^{-10} mol cm^{-2} sec^{-1} for the C60E. It is seen therefore that agreement is reasonably good between observed and calculated values.

From the above arguments on the effect of neglect of l_{12} and l_{23} it becomes obvious that both terms on the right hand side of equation 2.44 are underestimated.

$$J_s = \frac{-z_1 z_2}{r_1 r_2} \left(\frac{l_{11} l_{22} - l_{12}^2}{\alpha} \right) \left(-\frac{d\mu_{12}}{dx} \right) + \frac{1}{r_1} \left(l_{13} - \frac{t_1 t_3 \alpha}{z_1} \right) \left(-\frac{d\mu_3}{dx} \right) \qquad (2.44)$$

but since the salt force X_{12} and that on water X_3 are of opposite sign their difference remains unaltered, illustrating once again the dependence of J_s on the transport number of the co-ion.

The aspect of salt diffusion has been discussed by Helfferich using a treatment based on the Nernst-Planck equations (2)(91).

In the sodium forms of the C60 system the ratios l_{13} / c_1 and

l_{23} /

Table 5.5

	External electrolyte (0.1N at 25°C)	Membrane C60N	Membrane C60E
$\frac{L_{13}}{c_1} \times 10^{12}$	NaCl	16.3	35.0
$\frac{L_{23}}{c_2} \times 10^{12}$	NaCl	66.2	206
$\frac{l_{13}}{c_1} \times 10^{12}$	$CaCl_2$	5.78	16.6
$\frac{l_{23}}{c_2} \times 10^{12}$	$CaCl_2$	13.6	295

$\frac{l_{ik}}{c_i}$ units of mol J^{-1} cm^{-2} s^{-1}

L_{ik} and l_{ik} are the mobility coefficients referring to the sodium and calcium forms respectively.

L_{23} / c_2 are of the same order of magnitude showing that sodium and chloride ions have a similar coupling with water when adjustment is made for the concentration differences which exist in the membrane (43). These coupling interactions may be compared in terms of the Equivalent Valency Model introduced above with those observed for the calcium form. The identities

$$L_{13} = 2l_{13} \text{ and } L_{23} = l_{23}$$

have been established above, where L_{ik} and l_{ik} represent the univalent and divalent forms respectively. Therefore, for equinormal situations the relationship

$$\frac{l_{13}}{c_{Ca^{2+}}} \approx \frac{L_{13}}{c_{Na^{+}}} \approx \frac{L_{23}}{c_2}$$

would be expected. Table 5.5 shows however that the model overestimates l_{13} by about 100% in the expanded membrane C60E and this is also the case for the normal C60N. It would appear, therefore, that the calcium counterion-water coupling interaction is lower than would be expected on the basis of the model. Examination of the relative magnitudes of l_{13} / c_1 and l_{23} / c_2 (for the calcium form) supports this conclusion. l_{13} / c_1 and l_{23} / c_2 were calculated using the approximation $l_{12} = 0$ to be 5.78×10^{-12} and 13.63×10^{-12} mol J^{-1} cm^{-2} s^{-1} for the C60N membrane and 16.6×10^{-12} and 2.95×10^{-10} mol J^{-1} cm^{-2} s^{-1} in the C60E. l_{13} / c_1 for the C60N has a value approximately equal to half that of l_{23} / c_2. This relationship is not repeated in the C60E membrane but it has been noted above that l_{23} values are extremely susceptible to experimental uncertaintities.

For physical interpretation, the direct mobility coefficients are divided by a concentration term l_{ii} / c_i, where c_i is the concentration of species i, is known as an "intrinsic" mobility. In the membrane system this contains a large obstruction contribution due mainly /

Table 5.6

Intrinsic Mobilities. External solution 0.05m$CaCl_2$

Membrane	C60N			C60E		
Assumption	$l_{12}=0$	$l_{23}=0$	$R_{23}=0$	$l_{12}=0$	$l_{23}=0$	$R_{23}=0$
$\frac{l_{11}}{c_1} \times 10^{10}$	3.165	3.164	3.163	6.787	6.769	6.755
$\frac{l_{22}}{c_2} \times 10^{9}$	1.960	1.934	1.888	3.107	2.641	2.630
$\frac{l_{33}}{c_3} \times 10^{8}$	2.429	2.247	2.245	9.760	4.091	3.991

mainly to diffusion path tortuosity (as discussed in section 4.2.1).

When i = 1 or 2, l_{ii} / c_i includes smaller effects such as coulombic interaction of other i-type ions, solvation and frame of reference interactions. The intrinsic mobilities are shown in table 5.6 for both counterion, 1, and co-ion 2, species in the C60N and C60E membranes. The increased ease with which ions pass through the expanded membrane is again reflected. This is especially evident in the co-ion case in which, although c_2 is greater in the expanded membrane (3.14 mmol ml^{-1} for the C60N and 6.83 mmolml^{-1} for the C60E), its intrinsic mobility is increased.

Since in the system being investigated the frame of reference is matrix-fixed the intrinsic mobility of water, 3, may be determined.

Reference to table 5.6 shows that in both membranes the intrinsic mobilities increase in the order l_{11} / c_1 less than l_{22} / c_2 less than l_{33} / c_3.

In the solution analogue the chloride ion is large and order-destroying whereas the calcium ion with its higher charge density is order-producing. The drag effect of the electrophoretic and relaxation terms and the solution effect will therefore cause calcium to be much less mobile than chloride. It has been suggested that the solvation effect is small in the membrane system (section 2.5.1). However, as discussed above, the intrinsic mobilities must now contain a contribution due to interactions with the frame of reference (the matrix-fixed sulphonate group).

5.3.2 Discussion of R_{ik} Coefficient Values: Agreement between sets a,b and c is good for all major parameters. The co-ion is a minor component of the system and the largest discrepencies are as expected for the co-ion frictional coefficients R_{21}, R_{23} and R_{24}. Since the

R - /

R - coefficients in "d" do not correspond closely with those of the other groups some doubt is cast on the applicability of the "Spiegler" approximation $R_{22'} = 0$ to this system (further discussion as to the magnitudes of the isotope-isotope interactions is to be found in section 5.4).

The more open structure of the expanded membrane is reflected in the relative magnitudes of the R - coefficients. Reference to table 5.2 shows that frictional interaction between species in the expanded membrane is smaller than between the corresponding species in the normal.

The significance of the sign R - coefficients is discussed in Chapter 2 (section 2.4.4). The signs of the direct coefficients R_{ii} are positive as required by theory. Table 5.2 shows that R_{33} is negative for C60E using the approximation $R_{22'} = 0$. This is a further indication that the assumption $R_{22'} = 0$ is not valid for the system under investigation. R_{23} is particularly sensitive to the approximations chosen.

Cross coefficients are found to be both positive and negative. The frictional coefficients between counterion and water, R_{13}, and between counterion and matrix, R_{14}, are both negative implying on the basis of Kedem's observation (27) that there is an attractive force between the interacting species. Conversely, positive coefficients should indicate net repulsion between the interacting species. Coefficients R_{12} (counterion-to-co-ion interaction) and R_{24} (co-ion-to-matrix interaction) are found to be positive and negative respectively. These two results are not consistent with Kedem's intuitive suggestion since counterion-to-co-ion interaction would be expected to attract and the matrix-fixed sulphonate-to-co-ion interaction repulse. Indeed, previous work on the sodium form of the AMF C60 membranes (43) and studies by Meares (92) have indicated that Kedem's /

TABLE 5.7

Comparison of R- coefficients of the Sodium and Calcium Forms of the C60E membrane in terms of the hypothetical Equivalent Valency Model (the internal normality of the membranes is approximately 2N).

	sodium form		calcium form	
	observed	tortuosity correction (M)	observed	tortuosity correction (M)
R_{22} x10-12	102	13.92	55.46	5.85
R_{11} x10-12	0.830	0.113	4.04	0.427
R_{44} x10-12	0.602	0.0821	1.195	0.126
R_{33} x10-12	0.0013	0.000177	0.00129	0.000136
R_{12} x10-12	1.65	0.225	0.356	0.0375
R_{14} x10-12	-0.283	-0.0386	-1.33	-0.140
R_{13} x10-12	-0.0218	-0.00297	-0.0271	-0.00286
R_{23} x10-12	-0.102	-0.0139	-0.00239	-0.000252
R_{43} x10-12	-0.0128	-0.00175	-0.0200	-0.00211
R_{24} x10-12	-2.19	-0.299	-0.565	-0.0597

The above (M) tortuosity correction is obtained by dividing the observed results by M which is a tortuosity factor evaluated and discussed in Chapter 6 (table 6.3).

TABLE 5.7 (contd.)

Equivalent Valency Model comparisons for the C60E membrane. The predicted and observed $\frac{\tilde{R}_{ik}}{R_{ik}}$ values are tabulated (where $\tilde{R}_{ik}$ and R_{ik} represent the sodium and calcium forms respectively).

	observed	predicted
$\frac{\tilde{R}_{22}}{R_{22}}$	2.38	1.0
$\frac{\tilde{R}_{11}}{R_{11}}$	0.26	0.25
$\frac{\tilde{R}_{44}}{R_{44}}$	0.65	1.0
$\frac{\tilde{R}_{33}}{R_{33}}$	1.30	1.0
$\frac{\tilde{R}_{12}}{R_{12}}$	6.0	0.5
$\frac{\tilde{R}_{14}}{R_{14}}$	0.275	0.5
$\frac{\tilde{R}_{13}}{R_{13}}$	1.03	0.5
$\frac{\tilde{R}_{23}}{R_{23}}$	55.2	1.0
$\frac{\tilde{R}_{43}}{R_{43}}$	0.83	1.0
$\frac{\tilde{R}_{24}}{R_{24}}$	5.01	1.0

Kedem's observations may not hold for membranes.

Once again it is useful to refer to the hypothetical model described in section 5.12. In table 5.7 the individual R - coefficients for the sodium and calcium forms of the C60E system are correlated and compared when appropriate path tortuosity corrections have been made. The C60E membranes are compared since their internal normalities are almost equal at 2N. The direct frictional coefficient R_{11} for the calcium form is predicted accurately by the model as is R_{33} when corrections have been made for the differing ϵ_3 values in the sodium and calcium forms (table 4.1). R_{44} is overestimated by some 30% because it is calculated from eqn2.23.

$$\sum_{i=1}^{4} c_i R_{ik} = 0 \qquad (k = 1, \cdots 4) \qquad (2.23)$$

and the equation contains the term R_{14} which has been overestimated by a similar amount and R_{34} which is predicted accurately ($c_2 R_{24}$ in this instance is negligibly small). The cross coefficient R_{13} is underestimated by about 100% and these coefficients directly involving the co-ion, R_{12} R_{23} and R_{24} all show poor correspondence. Indeed, the direct coefficient R_{22} is overestimated by some 200-300%. It must be remembered however that the co-ion uptake of the membrane increases as sodium ions are replaced by calcium (for equinormal external concentrations, 0.1N, the co-ion concentrations c_2 of the C60E are 5.2×10^{-3} and 6.83×10^{-3} mol l^{-1} respectively for sodium and calcium forms).

Such variations in concentration must be considered when specific frictional interactions are compared. A more meaningful comparison would therefore be between the path tortuosity corrected $c_2 R_{22}$ values, and reference to table 5.7 will show that agreement is /

Table 5.8

Analysis of Frictional Interaction

Membrane	Ext Sol^{n}.	Total Friction c_1R_{11} x10^{-9}	=	Ion-water $-c_3R_{13}$ x 10^{-9}	Ion-matrix $-c_4R_{14}$ x10^{-9}
C60N	0.05mCaCl$_2$	3.671	=	0.918(25%)	2.754(75%)
C60E	0.05mCaCl$_2$	1.689	=	0.505(30%)	1.188(70%)
C60N	0.1mNaCl	0.990	=	0.569(58%)	0.425(43%)
C60E	0.1mNaCl	0.781	=	0.482(62%)	0.304(39%)

		$\frac{c_4R_{44}}{x10^{-9}}$	=	$\frac{-c_3R_{34}}{x10^{-9}}$	$\frac{-c_1R_{14}}{x10^{-9}}$
C60N	0.05mCaCl$_2$	1.750	=	0.364(21%)	1.382(79%)
C60E	0.05mCaCl$_2$	0.952	=	0.351(37%)	0.599(63%)
C60N	0.1mNaCl	0.857	=	0.431(51%)	0.426(50%)
C60E	0.1mNaCl	0.574	=	0.304(53%)	0.278(48%)

Membrane	Ext Sol^{n}.	Total Friction c_3R_{33} x10^{-7}	Counterion Water $-c_1R_{13}$ x10^{-7}	Matrix-water c_4R_{43} x10^{-7}

C60N /

Table 5.8 (contd.)

Membrane	Ext.Sol^{n}.	Total Friction c_3R_{33} x10^{-7}	Counterion-Water $-c_1R_{13}$ x10^{-7}	Matrix-Water c_4R_{43} x10^{-7}
C60N	0.05m$CaCl_2$	5.045	2.809(56%)	2.233(44%)
C60E	0.06m$CaCl_2$	2.334	0.974(42%)	1.347(58%)

is so much better between the sodium and calcium forms of the C60E membrane.

In this system c_1R_{11} measures the total frictional interaction between one mole of calcium and all other species per unit volume (ml) in its vicinity (89) and c_4R_{44} measures a similar quantity for the matrix-bound sulphonate ion. Study of similar systems (43) has shown that when the counterion is the monovalent sodium c_1R_{11} and c_4R_{44} are of similar magnitude, when the counterion was calcium, c_1R_{11} was twice as large as c_4R_{44} (table 5.8). These results are consistent with those of the sodium since in the calcium case the counterion is divalent.

Comparison between the sodium and calcium forms of the C60 membranes was extended by examining the proportions of each of the total frictional interactions c_1R_{11} and c_4R_{44} which are due to interactions with individual membrane components (table 5.8). These have been calculated for the calcium forms from equation 2.23 using R-coefficient values from table 5.2 (sets a,b, and c). It is evident that the contribution due to co-ion interactions is extremely small and it may therefore be ignored. In each membrane the total frictional interaction for the calcium counterion and for sulphonate-matrix is divided between ion-water and ion-matrix interactions in a ratio of approximately 1-4. When the counterion is sodium however the corresponding ion-water and ion-matrix interactions are of similar magnitude. It is possible therefore that ion association in some form is occurring between the calcium ions and the matrix-fixed sulphonate. Ion-matrix interactions have been examined in p.m.r. and Raman spectroscopic studies (78)(93)(94)(95)(96)(97). No indication of covalent character has been observed although these methods would not detect ion-pair formation by electrostatic bonding.

Evidence /

Evidence that site bonding appears to exist between polyelectrolytes containing sulphonate groups and calcium ions has been gathered by Strauss and Leung(98). The possibility that calcium-sulphonate ion association exists in the C60 membrane is investigated fully in section 6.2 in which the individual interactions in both sodium and calcium forms are compared with those of the solution analogues sodium chloride and calcium chloride.

A similar analysis of c_3R_{33} (table 5.8) shows that the total friction between one mole of water and all other species in unit volume of the membrane consists almost entirely of counterion-water and matrix-water interaction in approximately equal proportions.

Coupling coefficients (q) provide another method of studying the various individual interactions. These were defined by Kedem and Caplan (99) for a two-flow system,

$$q_{12} = \frac{l_{12}}{\sqrt{l_{11}\ l_{22}}} = \frac{-R_{12}}{\sqrt{R_{11}\ R_{22}}} \qquad (5.3)$$

and were subsequently extended by Caplan (100)(101) to multiple-flow systems.

$$q^*_{ij} = \frac{l_{ij}}{\sqrt{l_{ii}\ l_{jj}}} \qquad (5.4a)$$

$$q_{ij} = \frac{|R_{ij}|}{\sqrt{R_{ii}\ R_{jj}}} \qquad (5.4b)$$

where $q^*_{ij} \neq q_{ij}$ and $|R_{ij}|$ is the modulus of R_{ij}.

The coupling coefficient gives a quantitive measure of the degree of coupling between the flows of species i and j. Thus if q^*_{ij} or q_{ij} is zero then a flow of i would have no effect on j and if q^*_{ij} or $q_{ij} = 1$ there would be a complete coupling between the flows.

To /

Table 5.9

Coupling Coefficients Values

Coupling Coefficient	C60N	C60E
q_{13}	0.373	0.353
q_{14}	0.770	0.665
q_{34}	0.304	0.134

To obey the O.R.R. q^{*}_{ij} and q_{ij} must not exceed unity. Since mobility coefficient values are dependent on the frame of reference (9)(24) q^{*}_{ij} values contain a contribution from the source. However, R-coefficients are uniquely specified and so therefore are q_{ij} values. The coupling coefficients q_{13}, q_{14}, and q_{34} are evaluated and shown in table 5.9. These coefficients again reflect that in both C60N and C60E membranes the counterion matrix coupling is greatest. The q_{14} coupling coefficient is in fact greater than the total ion-water interactions (q_{13}). It is also noted that q_{13} exceeds q_{34}. The explanation for this may lie in the relative charge densities of the calcium and sulphonate ions. The calcium ion which has a high charge density is an order-producing ion and association with water molecules (solvation) is thermodynamically favourable. The sulphonate group, on the other hand, is a large order-destroying anion with a diffuse electrostatic charge and is therefore unsuited for coupling with water molecules.

5.4 Isotope - Isotope Interactions: The isotopic diffusion coefficient D_{ii} of a species i' may be represented as

$$D_{ii} = \frac{RT}{c_i \ (R_{ii} - R_{ii'})} \qquad (2.55)$$

Spiegler, as stated previously (section 2.45) used the assumption $R_{ii'} = 0$ in his theoretical derivation of X_{ik} frictional coefficients. This approximation has been used for $R_{22'}$ in previous studies of the sodium forms of C60 membranes (43). It was found as would be expected from the low co-ion concentration, c_2, in these membranes (c_2 is 2.4×10^{-3} and 5.2×10^{-3} moles l^{-1} for the C60N and C60E) to give results which agreed extremely well with those of several other approximations. In this work, however, the assumption $R_{22'} = 0$ has been /

been applied with less success (table 5.2) particularly in the C60E membrane which has a higher co-ion concentration (table 4.1). Another factor to be considered is discussed previously (section 4.2.3). It has been proposed (85) that co-ions tend to concentrate in regions of low charge density with the result that their frictional interaction, when considered on a mole to mole basis, will be larger than predicted from experimental data. Comparison of R_{22} coefficients calculated using various assumptions (table 5.2) shows that $R_{22'}$ is indeed a significant fraction of R_{22} (about 10% and 12% for C60N and C60E respectively depending on the assumption made).

The coefficients $R_{11'}$ and $R_{33'}$ have been shown experimentally to be of comparable magnitude to R_{11} and R_{33} respectively. Since there is a high concentration of counterion in the membranes (table 4.1) it is not surprising that in each case $R_{11'}$ and R_{11} are of comparable magnitude (table 5.2). It is however interesting to note that in both membranes $R_{11'}$ is negative. This is a direct contradiction of Kedem's Rule (27) since $R_{11'}$ is a measure of counterion-counterion interactions and as such would be expected to be positive. This result has been noted for other systems (43)(106) and although analogous solution studies (22)(73)(74) have yielded positive values for $R_{11'}$ it would appear to be a real rather than an apparent effect. The counterions in the membrane tend to be concentrated in regions around the matrix-polymer chains where there is little co-ion. As the counterion concentration in these regions increases all other species will become proportionately less significant so that a situation is approached in which only counterion-counterion interaction occurs. As the relative concentration of the species 2, 3 and 4 decreases counterion diffusion would still occur normally, and since $c_1 R_{11}$ would tend to zero, $R_{11'}$ must be negative to ensure a positive diffusion coefficient./

Table 5.10

Isotope-Isotope Interactions

Water

membrane	R_{33} x10^{-10}	$R_{33}-R_{33'}$ x10^{-10}	$R_{33'}$ x10^{-10}	$\frac{-c_3 R_{33'}}{c_3(R_{33}-R_{33'})}$
C60N	0.363	3.45	-3.078	0.892
C60E	0.129	1.65	-1.521	0.922

Counterion

membrane	R_{11} x10^{-12}	$R_{11}-R_{11'}$ x10^{-12}	$R_{11'}$ x10^{-12}	$\frac{-c_1 R_{11'}}{c_1(R_{11}-R_{11'})}$
C60N	8.424	15.660	-7.236	0.462
C60E	4.037	7.780	-3.743	0.481

coefficient.

The ratio $-R_{11'}/R_{11} - R_{11'}$ (table 5.10) shows what fraction of the the total resistance to counterion diffusion is due to counterion- to-counterion friction. When expressed as a percentage, it is seen that 46.2% in the C60N and 48.1% in the C60E of the total resistance is due to this interaction, and therefore 53.8% and 51.9% for the C60N and C60E respectively is attributed to interaction of the counterion with co-ion, water and matrix.

The $R_{33'}$ coefficient, when calculated from eqn 2.55 is found to be negative for both membranes (table 5.10). Table 5.10 shows that, for the C60N and C60E, 89.2% and 92.2% of the total resistance to water diffusion is due to water-to-water interactions and only 10.8% and 7.8% respectively to interactions with ions and matrix. In pure water-solvent the term c_3R_{33} is zero and sole contribution to water diffusion is water-water friction (which again must have a negative sign to ensure normal diffusion). Again force of attraction would be expected to cause concurrent flow of other water molecules.

In the light of this evidence along with that discussed in section 4.2.2 it is concluded therefore that the kinetic character of water interactions in the membrane is similar to those in pure water. The major effective contribution of the matrix to water diffusion appears therefore to be geometric rather than chemical or physical interactions and incorporated in a tortuosity factor.

5.5 Comparison of Nernst-Planck and Irreversible Thermodynamics: The predictive value of the Nernst-Planck Theory may be investigated by applying it to the complete set of transport data obtained for the calcium form of both C60N and C60E membranes.

It has been shown in chapter 2 (section 2.5.1) that the specific conductivity /

Table 5.11

Predicted and Observed Electrical Transport Results

		C60N	C60E
Specific cond. K $\times 10^2$ ($ohm^{-1}cm^{-1}$)	observed	0.521	1.10
	calculated	0.532	0.806
t_1	observed	0.989	0.982
	calculated	1.005	0.833
t_2	observed	0.011	0.018
	calculated	0.004	0.005

The observed results above were measured for an equilibrium solution of 0.05m $CaCl_2$ at 25°C. The calculated values of K and t_i were found using equations 2.81 and 2.82 respectively.

conductivity (K)and transport numbers (t_i) may be expressed as functions of the self-diffusion coefficients $D_{11}D_{22}$ and t_3,

$$K = \frac{F^2}{RT} \left\{ \frac{\sum_i Z_i^2 c_i D_{ii}}{1 + Z_4 c_4 t_3 / c_3} \right\} \tag{2.81}$$

$$t_i = \frac{F^2 Z_i^2 c_i D_{ii}}{RTK} + \frac{t_3 c_i Z_i}{c_3} \tag{2.82}$$

The specific conductivities and transport numbers of membranes C60N and C60E were calculated using equations (2.81) and (2.82) and tabulated as shown (table 5.11)along with the experimentally observed values. In the case of the C60N membrane the specific conductivity and counterion transport numbers were overestimated while t_2 was underestimated. All three transport values were however greatly underestimated in the case of the C60E membrane. To explain these effects a comparison was made between the Nernst-Planck and Irreversible Thermodynamics approaches.

The flows of counterion and co-ion may be presented in terms of the mobility coefficients using the derivation shown in section 2. The equations are

$$J_1 = \left\{ Z_1 l_{11} - Z_1 \frac{c_1 l_{11'}}{c_{1'}} + \frac{c_1}{c_3} (Z_1 l_{13} + Z_2 l_{23}) \right\} F (-\text{grad}\,\psi) \tag{2.86a}$$

$$\text{and } J_2 = \left\{ Z_2 l_{22} - Z_2 \frac{c_2 l_{22'}}{c_{2'}} + \frac{c_2}{c_3} (Z_1 l_{13} + Z_2 l_{23}) \right\} F (-\text{grad}\,\psi) \tag{2.86b}$$

The corresponding equations from Irreversible Thermodynamics are (using equations 2.30a and 2.30b)

$$J_1 = (Z_1 l_{11} + Z_2 l_{12}) F (-\text{grad}\,\psi) \tag{2.83a}$$

and /

Table 5.12

Comparison of Nernst-Planck and Irreversible Thermodynamic Estimates of l_{12} and l_{12}^*

	C60N	C60E
$\frac{c_1 D_{11}}{RT} \times 10^{13}$	0.639	1.285
$l_{11} \times 10^{13}$	1.383	2.887
$\frac{z_1 c_1 l_{11}}{c_{1'}} \times 10^{13}$	1.488	3.204
$z_2 l_{12} \times 10^{13}$	0.00042	0.0159
$\frac{c_1}{c_3}(z_1 l_{13}+z_2 l_{23}) \times 10^{13}$	1.537	2.345
$(z_2 l_{12})^* \times 10^{13}$	0.049	-0.859
$\frac{c_2 D_{22}}{RT} \times 10^{13}$	0.067	0.203
$l_{22} \times 10^{13}$	0.0607	0.180
$\frac{z_2 c_2 l_{22'}}{c_{2'}} \times 10^{13}$	0.0063	0.023
$z_1 l_{21} \times 10^{13}$	-0.00084	-0.031
$\frac{c_2}{c_3}(z_1 l_{13}+z_2 l_{23}) \times 10^{13}$	0.0110	0.0376
$(z_1 l_{21})^* \times 10^{13}$	0.0037	0.0146

and $J_2 = (Z_2 l_{22} + Z_1 l_{21})\, F\, (-\text{grad}\psi)$ (2.83b)

Comparing equations 2.86a and 2.86b with 2.83a and 2.83b shows

$$Z_2 l_{12} = - Z_1 c_1 \frac{l_{11'}}{c_{1'}} + \frac{c_1}{c_3} (Z_1 l_{13} + Z_2 l_{23}) \quad (2.87a)$$

and $$Z_1 l_{21} = -Z_2 c_2 \frac{l_{22'}}{c_{2'}} + \frac{c_2}{c_3} (Z_1 l_{13} + Z_2 l_{23}) \quad (2.87b)$$

As discussed above the O.R.R. is therefore destroyed. It is noted that while the isotopic term $c_i \frac{l_{ii'}}{c_{i'}}$ is positive (table5.12) for the counterion it is recorded as negative for the co-ion. In the co-ion case, however, $l_{22'}$ represents only a 10% fraction of l_{22}. Evaluation of $l_{22'}$ involves the values l_{22} and c_2. l_{22} is obtained from the co-ion transport number which has an experimental error of $\pm$ 8% while c_2 the co-ion concentration may be determined to within $\pm$ 5% (section 3.8). It is possible therefore that $l_{22'}$ may vary from negative to positive within the limits of experimental error.

In table 5.12the values $(Z_2 l_{12})^*$ and $(Z_1 l_{21})^*$ are equal to the right hand side of equations 2.87a and 2.87b respectively. It is noted that, in the case of the counterion, $Z_2 l_{12}$ is less than $(Z_2 l_{12})^*$ for the C60N, and $Z_2 l_{12}$ is positive while $(Z_2 l_{12})^*$ is negative for the C60E membrane. It therefore follows that the Nernst-Planck theory overestimates the counterion flow, J_1, in the C60N and underestimates J_1 in the C60E membrane.

The underestimation of t_2 in both membranes is rationalised because a positive $Z_1 l_{21}$ value has the effect of lowering t_2 (if Z_2 is negative as in this system) since,

$$t_2 = \frac{(Z_2 l_{22} + Z_1 Z_2 l_{21})}{K} F^2 \quad (2.30b)$$

Further /

Further reference to table 5.12 shows that while the positive values of $(Z_1 l_{21})^*$ obtained using the Nernst-Planck theory result in an underestimation of t_2 in both membranes this is much more marked in the C60E than in the C60N where the difference between $Z_1 l_{21}$ and $(Z_1 l_{21})^*$ is greater.

Similar comparisons have been made using different systems (30) (31) and these have shown that the effect produced in the C60N appears to be quite general. The results obtained for the C60E membrane may however be attributed to its high co-ion uptake (c_2 is 6.83 X 10^{-3} mole l^{-1}). It is seen immediately from equation (2.87b) that the high c_2 produces a large $(Z_1 l_{21})^*$ value. It has been argued above (section 5.2) that as c_2 increases the reducing effect of l_{23} and t_3 increases. The outcome is that eventually $\frac{Z_1 c_1 l_{11'}}{c_{1'}}$ exceeds $\frac{c_1}{c_3}(Z_1 l_{13} + Z_2 l_{23})$. In this event a negative sign is conferred on $(Z_2 l_{12})^*$ (table 5.12).

5.6 Hyperfiltration Studies: As outlined previously the results obtained in the hyperfiltration experiments (section 3.15) were used to assess the mobility coefficients calculated by applying the assumptions described above.

The mobility coefficients of equations 2.45a and 2.45b

$$J_s = L^1_{ss} X_s + L^1_{s3} X_3 \qquad (2.45a)$$

$$J_3 = L^1_{3s} X_s + L^1_{33} X_3 \qquad (2.45b)$$

were evaluated using the l_{ik} values obtained from the assumption $l_{12} = 0$ (section 5.1.1 , table 5.1). This assumption was chosen since it should provide the best value for the counterion - to-water mobility coefficient, l_{13}, and it is the accuracy of this coefficient which is of prime importance when used in conjunction with X_3.

Fluxes/

Table 5.13

Calculated salt and water fluxes, J_s and J_3 for the C60 membranes under 400 psi (2.76×10^6 Nm^{-2}) pressure at 25°C.

C60N membrane.

c_p(m)	X_3 x10^{-3}	X_{12} x10^{-4}	J_s x10^{11}	J_3 x10^7	$\frac{J_s}{J_3}$ 55.5
0.020	1.850	18.04	43.49	5.748	0.0420
0.025	1.871	13.06	35.97	5.767	0.0320
0.0306	1.893	8.575	29.23	5.796	0.0280
0.035	1.910	5.566	24.74	5.825	0.0236
0.040	1.930	2.635	20.38	5.860	0.0193

C60E membrane

c_p(m)	X_3 x10^{-3}	X_{12} x10^{-4}	J_s x10^{11}	J_3 x10^7	$\frac{J_s}{J_3}$ 55.5
0.020	1.843	16.53	290.5	39,25	0.0410
0.025	1.861	11.96	268.7	39.12	0.0381
0.0284	1.874	9.586	257.7	39.11	0.0365
0.0350	1.898	5.100	237.1	39.10	0.0337
0.040	1.916	2.414	225.1	39.17	0.0319

Units of J_s and J_3 are moles cm^{-2} sec^{-1}.

Units of X_3 and X_{12} are joules $mole^{-1}$ cm^{-1}.

J_s and J_3 values were calculated from equations 2.45a and 2.45b respectively using l_{ik} mobility coefficients obtained using the limiting assumption $l_{12} = 0$.

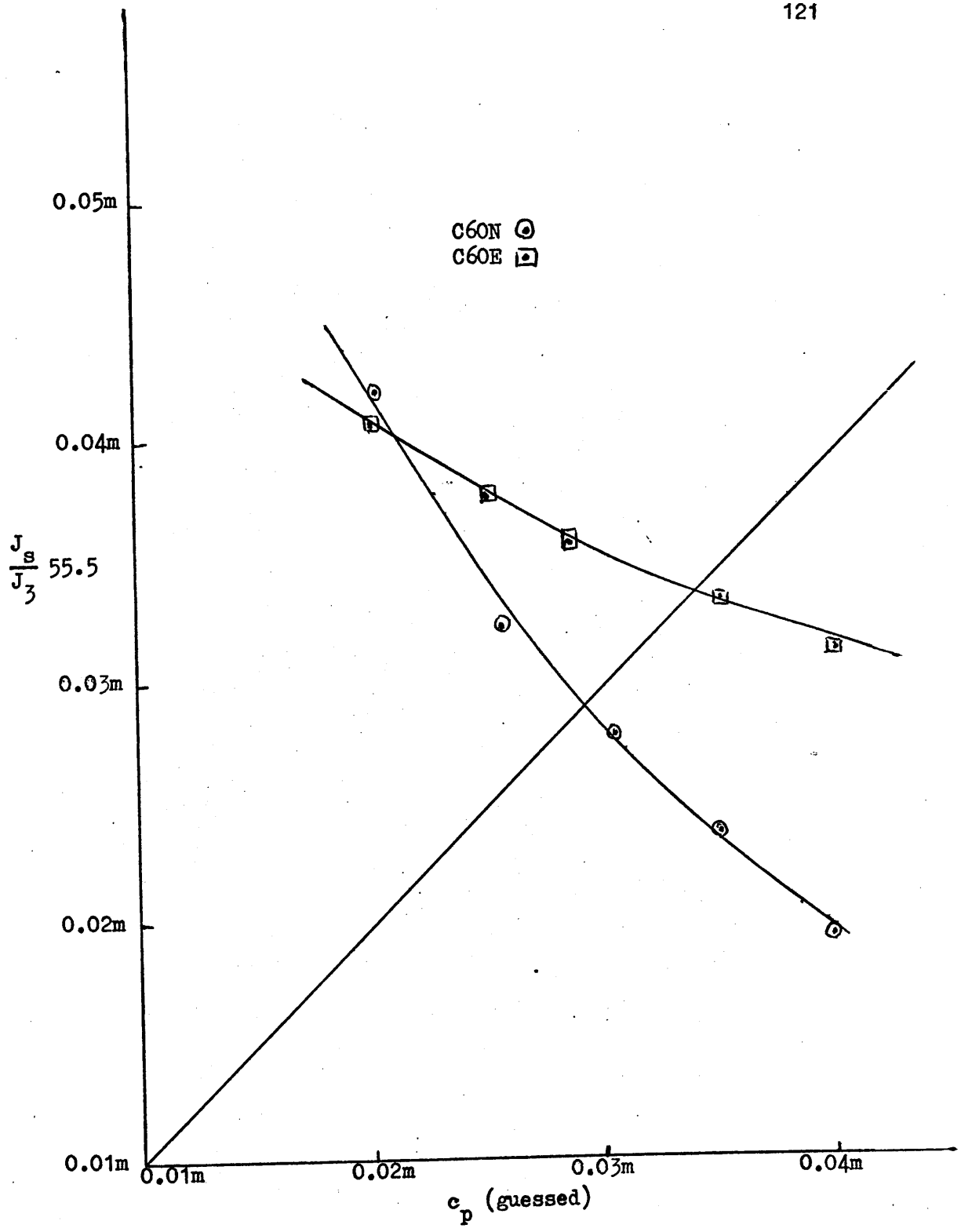

C60N
C60E
0.05m
0.04m
$\frac{J_s}{J_3}$ 55.5
0.03m
0.02m
0.01m
0.01m
0.02m
0.03m
0.04m
c_p (guessed)

Figure 5.1

Table 5.14

Comparison of calculated and observed values for water flux, J_3 and product concentration c_p(m).

C60N membrane

	Observed	Calculated
J_3(moles $cm^{-2}sec^{-1}$) x 10^7	11.8	5.245
c_p (molal)	0.0306	0.0290

C60E membrane

	Observed	Calculated
J_3(moles $cm^{-2}sec^{-1}$) x10^7	16.0	14.689
c_p (molal)	0.0284	0.0338

Calculated c_p values were obtained from figure 5.1 .

Fluxes J_s and J_3 were calculated for a range of product concentrations, c_p, which encompassed the observed value. Since $\frac{J_s}{J_3} c_3$ (where c_3 is the molality of water in the product solution) also defines the product concentration c_p, c_p(guessed) was varied until self-consistent results were obtained (figure 5.1 and table 5.13). In table 5.14 the observed results for membranes C60N and C60E are compared with those calculated using the l_{ik} coefficients described above. Fairly good agreement was obtained for the calculated and observed c_p values and it is noted that agreement is better for the C60N membrane. This may again reflect that the assumption used ($l_{12} = 0$) is applied more appropriately to the system containing the lower co-ion concentration.

CHAPTER 6

SALT MODEL CALCULATIONS

6.1 Introduction: Irreversible thermodynamics is a macroscopic discipline. Transport coeffients, obtained experimentally, cannot be calculated from molecular theory and the physical parameters of the system. The only exceptions appear to be very dilute electrolyte solutions in the range of the Onsager limiting law for electrical conductance (102). The interpretation and even the prediction of the membrane properties might be advanced if suitable and accessible analogous systems might be found.

The analogy between transport in an aqueous electrolyte and in a charged membrane might be considered. It has proved useful in earlier interpretations of thermodynamic problems such as selectivity (103). The most natural choice for a model would be the polyelectrolyte salt solution analogous to the cross-linked polyelectrolyte gel which constitutes the membrane. Imbibed electrolyte in the membrane would require the model to be a ternary electrolyte and transport could be compared at equal molalities in membrane and model. There are, however, insufficient data available on the transport properties of polyelectrolyte solutions and their ternary mixtures with simple salts to allow meaningful calculations at this time.

For the time being, therefore, model systems must remain more simple and are confined to limiting positions in which the properties of an ion exchange polymer membrane are assumed to be similar to those of a simple aqueous electrolyte. Extensive studies have been done concerning the observed properties of AMF C60 polystyrene sulphonic acid membranes in the sodium form containing sodium chloride as the invading salt (77). These were initiated by proposing that the sodium polystyrene sulphonic acid membrane may be modelled by an equimolal /

equimolal solution of sodium chloride. Although the theories developed were applied with apparent success to several membrane systems the salt model calculation presented below was developed primarily from observations on the C60 systems (43)(44)(77)(91). As stated above, this calculation was based mainly on the sodium forms of the C60 membranes but has proved successful for various ionic forms. Indeed much of this chapter will be devoted to salt model calculations for the calcium form of the C60 system with calcium chloride as invading salt and to comparison of the applicability of these calculations with those of the sodium form, at approximately equinormal concentrations. The AMF C60 membranes used are fully described in Chapter 2 and the physical and transport properties of the calcium forms of both C60N and C60E are detailed in Chapter 4.

The internal molality of the calcium forms of the C60N and C60E membranes in 0.05m $CaCl_2$ are 1.70 and 1.07 m respectively. Due to the unavailability of relevant transport data for aqueous calcium chloride solutions at concentrations exceeding 1.0 molar it was decided to use only the C60E membrane results for comparison with the solution analogue.

6.2 Salt Model Calculations: The salt model calculation is based upon the properties of a single electrolyte for which a complete irreversible analysis is available at concentrations which include the total ionic mobility exchanger.

Experimental evidence (31)(43) has shown that a similarity existsbetween the function of sulphonate-matrix-fixed charge in the C60 membrane and free chloride ion in solution and this suggests that chloride and sulphonate have similar kinetic behaviour. Since the co-ion for these studies is chloride a model may be conceived in which chloride of two "sorts" is present;chloride, species 2, which is the co-ion /

co-ion in the membrane, and chloride, species 4, which is fixed relative to the membrane matrix. These two forms are taken to be chemically identical but physically distinguishable isotopes. A precise definition is therefore allowed of the frictional and mobility coefficients of the ternary solution; in particular of the absolute magnitudes of R_{2i} and R_{4i} (i=1,2,3,4), the frictional coefficients between co-ion and fixed charge and the other components of the system.

This model implies that the polymer matrix has no chemical influence upon the transport process but, by virtue of its presence, obstructs diffusional pathways in the membrane phase and renders them tortuous. Major deviations between the predictions of the model and observed transport parameters can therefore be considered as indications of specific polymer effects and the possibility with certain ions that sulphonate and chloride may have quite different complexing or ion-pairing characteristics would obviously undermine the model. It might also be expected that dilute homogeneous membranes or membranes with significant voids would have local ionic distributions which were grossly different from those in a simple aqueous solution of equal molality and consequently the processes of transport would be polymer-dependent and specific processes such as polymer chain diffusion pseudo-mosaic effects would be significant.

If,however, the aqueous and ion-permeable regions of the membrane constitute an essentially homogeneous phase, it is conceivable that the distribution of charges might approximate to those in an aqueous electrolyte solution and in this range a salt model would predict membrane properties which were of the correct magnitude.

The choice of a salt model based on a ternary isotopic solution allows a precise evaluation of model coefficients. The theory of isotopic diffusion and the identification of isotope-isotope coefficients/

coefficients has been developed by Laity (104) and by Kedem and Essig (35). The treatment given below is mainly developed to express frictional interaction in the isotopic ternary solution in terms of those of the parent binary electrolyte and the isotopic diffusion coefficient for the co-ion.

Since the analysis requires a change of frame of reference from solvent, to ion-4-fixed in the membrane model, a development is presented using frictional coefficients, R_{ik}, which are independent of frame of reference.

The phenomenological equations (2.19) for a binary electrolyte (1,2) are given by eqn. (6.1) in which 1 represents the counterion and 2 the co-ion.

$$\begin{vmatrix} X_1 \\ X_2 \end{vmatrix} = \begin{vmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{vmatrix} \begin{vmatrix} J_1^3 \\ J_2^3 \end{vmatrix} \qquad (6.1)$$

The flows of counterion, J_1^3 and co-ion J_2^3 are given on a solvent-fixed frame of reference. Thermodynamic forces on a counterion and co-ion defined by the negative gradients of chemical potential are given by X_1 and X_2 respectively. In the ternary isotopic solution of equal concentration, some of co-ion,2, is replaced by co-ion,4, which is chemically identical in all respects such that the total co-ion concentration in the binary is the sum of the concentration of 2 and 4 in the ternary (equation 6.2),

$$C_2 = c_2 + c_4 \qquad (6.2)$$

The phenomenological equations for this ternary solution are given in eqn. 6.3 in which forces, frictional coefficients and flows are represented by lower case symbols x_i, r_{ik}, and j_i^3 respectively.

$$\begin{vmatrix} x_1 \\ x_2 \\ x_4 \end{vmatrix} = \begin{vmatrix} r_{11} & r_{12} & r_{14} \\ r_{21} & r_{22} & r_{24} \\ r_{41} & r_{42} & r_{44} \end{vmatrix} \begin{vmatrix} j_1^3 \\ j_2^3 \\ j_4^3 \end{vmatrix} \qquad (6.3)$$

From /

From eqns (6.1) and (6.3) the Onsager Reciprocal Relations will be assumed such that $R_{ik} = R_{ki}$ and $r_{ik} = r_{ki}$ for all i and k. (Extensions to relationships proved between R- and r- coefficients due to those identities will be represented by (+ O.R.R.)).

In a comparison of a binary solution (eqn 6.2) and the same solution in which an isotopic form of 2 is present (eqn 6.3) the following identities exist (eqns (6.4),(6.5),(6.6)),

$$J_1^3 = j_1^3 \; ; \quad J_2^3 = j_2^3 + j_4^3 \; ; \quad X_1 = x_1 \qquad (6.4)\ (6.5)\ (6.6)$$

and by using the Gibbs-Duhem relationship for forces in both systems eqn (6.7) is obtained,

$$C_2 X_2 = c_2 x_2 + c_4 x_4 \qquad (6.7)$$

Under conditions for isotopic diffusion of co-ion (eqn(6.3)) $x_1 = 0 = j_1^3$, and from eqns (6.3), (6.4) and (6.5),

$$r_{12} = r_{14} \quad (+0.R.R.)$$

Comparison of X_1 and x_1 in experiments without isotopic forces shows,

$$R_{11} = r_{11}, \text{ and } R_{12} = r_{12} = r_{14} \quad (+0.R.R.).$$

The coefficients r_{22}, r_{24} (r_{42}), and r_{44} of eqn (6.3) cannot be determined solely by comparison of coefficients in eqn(6.1) and (6.3) but are related to the isotopic diffusion coefficient for co-ion D_{22}(and D_{44}).

If a purely electrical force is applied to both solutions,

$$X_2 = x_2 = x_4 = Z_c \mathbf{F} (-\text{grad}\,\psi) \qquad (6.8)$$

where $Z_c = Z_2 = Z_4$ is the co-ion valency (including sign), and grad ψ is the local gradient of electrical potential. Comparison of expansions for X_2 and x_2 and x_4 gives eqns (6.9) and (6.10),

$$R_{22}J_2^3 = r_{22}j_2^3 + r_{24}j_4^3 \qquad (6.9)$$

$$\text{and } R_{22}J_2^3 = r_{42}j_2^3 + r_{44}j_4^3 \qquad (6.10)$$

Since/

Since co-ions 2 and 4 are chemically identical they will have the same electrochemical mobility, V^*, (cm s^{-1}) under unit electrical potential gradient. Since $J = C V^*$,

$$C_2R_{22} = c_2r_{22} + c_4r_{24} = c_2r_{42} + c_4r_{44} \qquad (6.11)$$

Under conditions for isotopic diffusion of co-ion eqn(2.18) is,

$$J_i = \sum_{k=1}^{3} l_{ik}X_k \qquad i=1,2,3. \qquad (2.18)$$

and the total force and total flow of co-ion are separately zero and from eqns (6.7) and (6.5),

$$c_2 x_2 = -c_4 x_4 \quad \text{and} \quad j_2^3 = -j_4^3 \qquad (6.12)$$

It is easily shown that the isotopic flows obey Fick's Law and that the isotopic diffusion coefficients of 2 and 4, D_{22} and D_{44} respectively, are equal (eqn(6.13)),

$$D_{22} = \frac{RT}{c_2(r_{22} - r_{24})} = \frac{RT}{c_4(r_{44} - r_{42})} \qquad (6.13)$$

From eqn 6.11 these diffusion coefficients may be expressed in terms of the direct frictional coefficients of co-ion in the binary R_{22} and the frictional coefficient between isotopes 2 and 4 in the ternary r_{24} (r_{42}), (eqn 6.14),so that,

$$D_{22} = D_{44} = \frac{RT}{c_2(R_{22} - r_{24})} \qquad (6.14)$$

The relative concentrations of co-ion isotopes, c_2 and c_4, are not required in this equation and the isotope-isotope frictional coefficient r_{24} (r_{42}) may be obtained directly from the self- or isotopic diffusion coefficient of the co-ion in solution and the corresponding values of R_{22} and C_2 in the binary.

From eqns (6.11) and (6.14) explicit expressions for the frictional coefficients r_{24} (r_{42}), r_{22} and r_{44} of eqn (6.3) are obtained, (eqns (6.15), (6.16) and (6.17)),

$$r_{24} = r_{42} = R_{22} - \frac{RT}{c_2D_{22}} \qquad (6.15)$$

r_{22}/

$$r_{22} = R_{22} + \frac{c_4}{c_2}\frac{(RT)}{(C_2D_{22})} \qquad (6.16)$$

and $$r_{44} = R_{22} + \frac{c_2}{c_4}\frac{(RT)}{(C_2D_{22})} \qquad (6.17)$$

These last two coefficients, r_{22} and r_{44}, depend upon the relative proportions of isotopes 2 and 4 in the solution.

From the identities,

$$\sum_{i=1}^{3} C_i R_{ik} = 0 \qquad k = 1,2,3 \qquad \text{and}$$

$$\sum_{i=1}^{4} c_i r_{ik} = 0 \qquad k = 1,2,3,4$$

applied to the phenomenological equations (6.1) and (6.3) respectively, it is easily shown that the ion-to-water frictional coefficients in the isotopic ternary are equal to those in the parent binary; eqn (6.16)

$$r_{22} = R_{22} + \frac{c_4}{c_2}\frac{(RT)}{(C_2D_{22})} \qquad (6.16)$$

$$R_{13} = r_{13} \text{ and } R_{23} = r_{23} = r_{43} \text{ ; (+ 0.R.R.)} \qquad (6.18)$$

Consequently,

$$R_{33} = r_{33}.$$

6.3 Phenomenological Equations relative to ion 4: Eqn (6.3) may be taken as a model for the exchanger membrane in which ion 4 represents the fluid charge in the polymer, and 2, the co-ion imbibed by the membrane from the external solution. Membrane flows are measured relative to the stationary matrix and therefore relative to the ion, species 4. On a "4-fixed" frame of reference the phenomenological equations (2.18) become eqn (6.19),

$x_1/$

$$\begin{vmatrix} x_1 \\ x_2 \\ x_3 \end{vmatrix} = \begin{vmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{vmatrix} \begin{vmatrix} j_1^4 \\ j_2^4 \\ j_3^4 \end{vmatrix} \qquad (6.19)$$

The flows j_i^4 are the flows of ions 1,2 and water, 3, relative to the fixed anion 4, where $j_i^4 = (j_i^3 - \frac{c_i}{c_4} j_4^3)$. All frictional coefficients, r_{ik}, are defined by the binary with the exception of r_{22}, which, from eqn. (6.16) is dependent on the isotopic diffusion coefficient D_{22} and the concentration ratio $\frac{c_4}{c_2}$. Thus the direct coefficient r_{22} is strongly dependent on the concentration of salt in the membrane and increases as co-ion uptake c_2 diminishes. This feature has been observed in experimental studies of ion exchange (43).

6.4 Scaling factors for transport parameters: Eqn. (6.19) is representative of a non-tortuous membrane in which no account has been taken of the presence of polymer. The model assumes that the membrane function is determined by the ionogenic fixed groups on the polymer, that these groups are similar to simple aqueous anions and that the polymer matrix has no influence on the movement of ions or water other than, by its presence, to restrict movement by constraining mobile species to tortuous diffusional pathways.

Concentrations in the membrane are usually expressed in moles cm^{-3} of total membrane volume, $\bar{c}$, where $\bar{c} = V_w c$ and V_w is the fractional aqueous volume (or pore volume) of the membrane. Flow across the membrane is referred to in terms of flow per unit area of exposed membrane, $\bar{J}$, so that $\bar{J} = j V_w'$ where V_w' is the ratio of "pore" to geometric area at the membrane surface. The membrane may be defined as homogeneous in macroscopic terms if $V_w' = V_w$.

The /

The presence of polymer in the membrane may be considered to increase the effective length of diffusional pathways across the membrane, such that a membrane of geometric thickness $\bar{d}$ may have a diffusional path length of $\bar{d}\,\theta$ which corresponds to a solution of path length d where $\theta > 1$ (θ is the tortuosity factor which is discussed in section 4.2.1).

Fick's equation for isotopic diffusion of co-ion may be chosen to illustrate these scaling effects (eqn.6.19).

$$J_2 = -D_{22} \frac{\Delta c_2}{d} \tag{6.20}$$

becomes $$\frac{\bar{J}_2}{V_w'} = \frac{-D_{22}}{\theta} \frac{\Delta \bar{C}_2}{d} \frac{1}{V_w} \tag{6.21}$$

and if $V_w' = V_w$ as in homogeneous membrane,

$$\bar{J}_2 = \frac{-D_{22}}{\theta} \frac{\Delta \bar{C}_2}{\bar{d}} \tag{6.22}$$

so that $$\frac{D_{22}}{\theta} = \bar{D}_{22} \tag{6.23}$$

The diffusion coefficient of co-ion in the tortuous membrane, $\bar{D}_{22} = \frac{D_{22}}{\theta}$ using this salt model calculation and so is smaller than in free solution. Using barred symbols to represent the membrane,

$$\bar{D}_{22} = \frac{RT}{\bar{C}_2 (\bar{R}_{22} - \bar{R}_{22'})} \tag{6.24}$$

and consequently

$$\bar{R}_{22} = \frac{r_{22}\,\theta}{V_w} \quad \text{and} \quad \bar{R}_{22'} = \frac{r_{22'}\theta}{V_w}$$

where 2' is the isotopic form of2 used in membrane co-ion diffusion (it is easily shown that $r_{22'} = r_{24}$). Since the analysis may be applied to/

to the forces and flows in the phenomenological eqns (6.19) it is true that,

$$\bar{R}_{ik} = r_{ik} \frac{\theta}{V_w} \tag{6.25}$$

or in inverse form as mobility coefficients l_{ik};

$$\bar{l}_{ik} = l_{ik} \frac{V_w}{\theta} \tag{6.26}$$

The value of the tortuosity coefficient calculated by theoretical estimations is dependent upon the statistical model of the exchanger phase chosen and values from independent theoretical models may not be consistent. In this study of the calcium form of the C60 membranes and in previous work on the sodium forms (43)(44)(91) Prager's estimate of the tortuosity factor θ_p and Meare's value of the path tortuosity θ_m have to be used.

The salt model calculation S.M.C. however defines θ as $\frac{D_{22}}{\bar{D}_{22}}$ and as θ it will be used in the comparisons of experimental membrane and S.M.C. parameters given below.

An estimate of the frictional coefficients for an experimental membrane may be therefore obtained from a knowledge of its physical dimensions, the concentrations of ions and water in the membrane and the co-ion diffusion coefficient. Before making comparisons of this sort it is useful to summarise the predicted correspondence between membrane $\bar{R}_{ik}$ and solution frictional parameters eqn (6.27) which is represented in matrix form,

$$\begin{vmatrix} \bar{R}_{11} & \bar{R}_{12} & \bar{R}_{13} & \bar{R}_{14} \\ \bar{R}_{21} & \bar{R}_{22} & \bar{R}_{23} & \bar{R}_{24} \\ \bar{R}_{31} & \bar{R}_{32} & \bar{R}_{33} & \bar{R}_{34} \\ \bar{R}_{41} & \bar{R}_{42} & \bar{R}_{43} & \bar{R}_{44} \end{vmatrix} = \begin{vmatrix} R_{11} & R_{12} & R_{13} & R_{12} \\ R_{21} & r_{22} & R_{23} & r_{24} \\ R_{31} & R_{32} & R_{33} & R_{32} \\ R_{21} & r_{42} & R_{23} & r_{44} \end{vmatrix} \frac{\theta}{V_w} \tag{6.27}$$

"membrane" (S.M.C.) — solution

where r_{22}, r_{44} and r_{24} $(=r_{42})$ are defined by eqns (6.16) and (6.17) and/

and (6.15) respectively.

6.5 Application of the S.M.C: Before making a detailed comparison between this simple model calculation and the observed properties of membranes it is of interest to note that the model predicts that a value of $\bar{R}_{22}$ may be obtained directly from the isotopic diffusion coefficient of co-ion in the membrane, $\bar{D}_{22}$, provided the ratio of fixed charge to co-ion concentration is large (eqns (6.13)(6.15)(6.16).) For most binary electrolytes the function RT/C_2D_{22} is of the same order of magnitude as R_{22}. For example, in aqueous calcium chloride of concentration 1M the function is some 10% smaller than R_{22}.

If the co-ion-to-sulphonate friction in the experimental membrane is even approximately equal to r_{24} of the salt model calculation,

$$\bar{R}_{22} \sim \frac{RT}{\bar{C}_2 \bar{D}_{22}} \qquad (6.28)$$

Again within the limits of applicability of the model the error in using eqn (6.21) would be approximately $10c_2/c_4\%$ in the membrane (at the molalities quoted).

There are certain consequences of the isotope model presented. The first is that, since co-ion and matrix-fixed charge,4, are taken to be chemically identical, the transport number of co-ion t_2 will be defined as zero. The change of frame of reference to membrane- or 4- fixed automatically requires co-ion to be stationary relative to 4 in an electrical experiment. Equally the value of the electro-osmotic transference number, t_3, will be identical to that obtained by considering the flow of water relative to all co-ions, fixed, in the binary so that,

t_3 /

TABLE 6.1a

Comparison of S.M.C. with experimental R-coefficients for C60E

The C60E membrane in 0.05M $CaCl_2$ and 0.1M NaCl

	Exptl. (l_{12}=0)	S.M.C.	S.M.C.xP	S.M.C.xM
Extn. soln.	0.1M NaCl	0.1M NaCl	0.1M NaCl	0.1M NaCl
R_{22} x10-12	102	14.024	82.9	103.0
R_{11} x10-12	0.83	0.134	0.79	0.98
R_{44} x10-12	0.602	0.0848	0.501	0.621
R^{o}_{22} x10-12		0.0848	0.501	0.621
R_{33} x10-12	0.0013	0.000261	0.0015	0.0019
$-R_{12}$ x10-12	-1.65	0.0203	0.120	0.149
$-R_{14}$ x10-12	0.283	0.0203	0.120	0.149
$-R_{13}$ x10-12	0.218	0.00436	0.0258	0.0320
$-R_{23}$ x10-12	0.102	0.00247	0.0145	0.0181
$-R_{43}$ x10-12	0. 0128	0.00247	0.0145	0.0181
R_{24} x10-12	2.19	0.0090	0.053	0.066

TABLE 6.1 b

	Exptl. (l_{23}=0)	S.M.C.	S.M.CxP	S.M.C.xM	S.M.C.xexp.
Extn. Soln.	0.05M $CaCl_2$	0.05M $CaCl_2$	0.05M $CaCl_2$	0.05M $CaCl_2$	0.05M $CaCl_2$
R_{22} x10-12	55.46	9.931	75.2	94.1	108.5
R_{11} x10-12	4.04	0.762	5.77	7.21	8.33
R_{44} x10-12	1.95	0.091	0.689	0.862	0.994
R^{o}_{22} x10-12		0.0904	0.688	0.861	0.992
R_{33} x10-12	0.00129	0.000285	0.00217	0.00271	0.00311
$-R_{12}$ x10-12	-0.356	0.073	0.554	0.693	0.798
$-R_{14}$ x10-12	1.33	0.073	0.554	0.693	0.798
$-R_{13}$ x10-12	0.0271	0.0114	0.0864	0.1082	0.1248
$-R_{23}$ x10-12	0.00239	0.00200	0.0151	0.0189	0.0219
$-R_{43}$ x10-12	0.0200	0.00200	0.0151	0.0189	0.0219
$-R_{24}$ x10-12	-0.565	0.011	0.0833	0.1042	0.1202

$$t_3 = -\frac{c_3}{z_2 c_2}\ t_2^3 = \frac{c_3}{z_1 c_1}\ t_2^3$$

where t_2^3 is the transport number for co-ion in the binary solution. The specific conductivity, K, is independent of the frame of reference chosen for the measurement and so the S.M.C. predicts the specific conductivity of the membrane $\bar{K}$ by eqn (6.29).

$$\bar{K} = K \frac{V_w}{\theta} \qquad (6.29)$$

For these parameters it is sufficient to know the co-ion transport number relative to water, t_2^3, and the specific conductivity of the model binary K to obtain predicted membrane parameters.

6.6 Observed and Calculated Membrane Parameters:

The Salt Model Calculation has been developed above as a general theory and its essential validity may be illustrated by referring to the sodium form of the C60 membranes (77). The frictional coefficients for the binary model electrolyte sodium chloride were obtained from Miller's tabulated data (28) and those for the binary model calcium chloride were calculated using primary data from references (86)(105). Since molarity, C, of species relative to unit volume of aqueous pore solution is not defined unequivocally, this concentration was estimated by assuming the ratio of molarity to molality in the membrane to be the same as in the corresponding equimolal aqueous chloride solution at 25°C. Since sufficient primary solution data for aqueous calcium chloride could be obtained at concentrations not exceeding one molar, comparisons were restricted to the expanded membrane C60E which had an internal molality in the calcium form of 1.07m.

Frictional coefficients obtained from experimental data and from the Salt Model Calculation (S.M.C.) are given in Tables 6.1a and 6.1b. Tortuosity corrections, $\frac{\theta}{V_w}$ have been estimated, using the ratio/

Table 6.3

Tortuosity corrections for membrane C60E in equinormal equilibrium solutions of NaCl and $CaCl_2$.

Membrane C60E

Ext^n. Sol^n.	0.05m$CaCl_2$	0.1m NaCl
θ_p	3.229	2.78
θ_M	4.04	3.45
θ_{exp}	4.66	3.44
P	7.57	5.91
M	9.47	7.33
exp	10.93	7.31

$P = \frac{\theta_p}{V_w}$; $M = \frac{\theta_M}{V_w}$; $exp = \frac{\theta_{exp}}{V_w}$. V_w is defined as the pore volume of the membrane

ratio $\frac{D_{22}}{D_{22}}$ as suggested by the model and those of Meares and Prager in the manner discussed above. These three methods, designated (exp), (M) and (P) respectively are shown in the tabulated data. (table 6.3).

The experimental frictional coefficients shown in table 6.1a are for the sodium form of the C60E and are determined using the approximation $l_{12}=0$(43). The agreement in table 6.1a between calculated and experimental coefficients R_{ik} is in general extremely good, with calculated values following in detail the trends and magnitudes found from data derived from experimental measurements (43)(91). The particularly close agreement between calculated and experimental values of R_{22} and R_{44} largely justifies the basic assumption of the Salt Model Calculation; that aqueous chloride and sulphonate-matrix anions have similar kinetic characteristics.

In table 6.1b the experimental frictional R-coefficients for the calcium form of the C60E membrane are calculated using the approximation $l_{23}=0$ as described in section 5.1.1. This approximation was chosen as being the one which gave most consistent results for the calculations used in the above chapter.

It is immediately obvious that the agreement between calculated and experimental values is much less good, although, on the whole, trends in observed data are still followed by the S.M.C. The direct coefficient R_{44} is fairly well approximated but those for calcium, R_{11}, water, R_{33}, and chloride, R_{22}, are all overestimated by the S.M.C. The coefficient R_{34} indicates that the water-sulphonate-matrix frictional interaction is similar to the water-chloride frictional interaction in the model. However R_{13}, the counterion-to-water frictional interaction, is greatly overestimated by the model while R_{14}, the counterion-sulphonate-matrix frictional interaction, is underestimated.

The /

TABLE 6.2

Comparison of S.M.C. with experimental values of l-coefficients for C60E membrane in 0.05m $CaCl_2$

Internal molality of membrane 1.07m

	C60E exptl. (l_{23}=0)	S.M.C.	$\frac{S.M.C}{P}$	$\frac{S.M.C}{M}$	$\frac{S.M.C.}{exp}$
l_{11} x10^{13}	2.89	32.60	4.30	3.34	2.98
l_{12} x10^{15}	-1.59	50.10	6.62	5.29	4.58
l_{22} x10^{14}	1.80	10.0	1.33	1.06	0.915
l_{13} x10^{11}	0.607	13.0	1.72	1.37	1.19
l_{23} x10^{13}		27.00	3.57	2.85	2.47
l_{33} x10^{9}	0.903	8.67	1.14	0.92	0.79

The major coefficients R_{13} and R_{14} have proved to be equally anomalous when the calcium forms of the C60 membranes are compared directly with the sodium forms (table 5.8) and possible reasons for these observations are suggestions and discussed at length in section 5.32.

Mobility coefficients l_{ik} for this system are shown in table 6.2. The model, by assuming identical co-ion and fixed charge, restricts the calculated co-ion transport number to zero so that from equation (2.30b)

$$t_2 = \frac{z_2^2 l_{22} + z_1 z_2 l_{12}}{\alpha} \qquad (2.30b)$$

$z_2^2 l_{22} = - z_1 z_2 l_{12}$ in the S.M.C.. For a 2:1 salt such as calcium chloride, $l_{22} = 2l_{12}$.

The direct mobility coefficients l_{11} and l_{33} are predicted with reasonable accuracy although no single tortuosity correction consistently gives best correspondence. The experimental value l_{12} is small and cannot be calculated with confidence for this system which has low co-ion uptake. Table 5.1 shows in fact that the application of the assumptions $l_{23} = 0$ and $R_{23} = 0$ results in negative values of l_{12}. The direct mobility of the co-ion, l_{22}, is underestimated by the Salt Model Calculation. The calculated value of the co-ion- to-water coupling coefficient l_{23} is about 2% of l_{13}. In this system with a 2:1 electrolyte the assumption $l_{23} = 0$ is therefore valid since this coefficient appears only in equation 2.32,

$$t_3 = \frac{z_1 l_{13} + z_2 l_{23}}{\alpha} \qquad (2.32)$$

which/

Table 6.4

S.M.C. Predictions for the C60E membrane in 0.05m $CaCl_2$

	Observed	Calculated
Transference Number (t_3)	10.30	19.88
Specific Conductivity (K) ($ohm^{-1}cm^{-1}$) $x10^2$	1.10	1.59((P)correction) 1.29((M)correction) 1.10((exp) ")
Water Flux(J_3) (mole $cm^{-2}s^{-1}$) $x10^8$	-11.48	-4.42((P)correction) -3.53((M) ") -3.06((exp) ")
Salt Flux(J_s) (mole cm^{-2} s^{-1}) $x10^{10}$	9.71	6.35((P)correction) 5.08((M) ") 4.40((exp) ")

which is the expression for the electro-osmotic transference number t_3. The counterion-to-water coupling coefficient l_{13} is greatly overestimated by the S.M.C. (table 6.2).

A basic requirement of the model is that co-ion diffusion in the membrane and model electrolyte differs solely due to tortuosity effects and reference to section 4.2 (table 4.3) will show that this requirement has been met.

6.7 Predictions of Experimental Measurements: Measured and predicted transport properties are given in table 6.4. The specific conductivity, K, is estimated accurately particularly with the (exp) tortuosity correction and this is a reflection of the accuracy to which the direct mobility coefficient l_{11} is predicted from the binary model (eqn 2.27 and eqn 6.29). The electro-osmotic transport number t_3 is overestimated by about 100%. This term, when calculated from the transport number of the co-ion, t_2^3, in the binary model, does not take account of co-ion movement in the membrane which will tend to reduce electro-osmotic flow. It is not suggested, however, that in this system consideration of co-ion movement in the membrane would reduce the calculated electro-osmotic flow by more than about 10%. The high predicted value of t_3 is reflected by the overestimation in the Salt Model of the counterion-water coupling coefficient term l_{13} (table 6.2 and eqn 2.32).

Salt and osmotic flows across the membrane were measured when a concentration gradient of 0.025m/ 0.075m was maintained across the membrane (section 3.11). For the S.M.C. these flows are given in equations 2.42 and 2.41 which become,

$J_s/$

TABLE 6.5

Salt Model - Water Transference Number Comparisons.

Membrane	C60N2	C60N2	C60N1
Electrolyte 0.1M	HCl	NaCl	LiCl
Wet weight (g)	0.3316	0.3220	0.2612
Capacity meg/disc	0.306	0.306	0.225
Wt. of counterion (g)	0.0003	0.0071	0.0016
Dry weight (g)	0.2161	0.2161	0.1850
Wt.of water (g)	0.1152	0.0988	0.0746
% water w.r.t dry wt. of matrix	50.02	44.7	40.32
$\frac{\text{conc. of water } (c_3)}{\text{conc. of counterion } (c_1)}$	20.92	19.94	18.40
t_2^3	0.150	0.644	0.714
$\frac{c_3}{c_1} t_2^3$	3.14	11.55	13.20
t_3(obs)	3.05	11.02	12.88

TABLE 6.5 (contd.)

Salt Model - Water Transference Number Comparisons.

Membrane	C60N1	C60N1	C60N1	C60N1
Electrolyte 0.1M	NaCl	KCl	RbCl	CsCl
Wet weight (g)	0.2569	0.2502	0.2585	0.2670
Capacity meg/disc	0.225	0.225	0.225	0.225
Wt. of counterion (g)	0.00052	0.0090	0.0194	0.0306
Dry weight (g)	0.1850	0.1850	0.1850	0.1850
Wt. of water (g)	0.0667	0.0562	0.0541	0.0514
% water w.r.t. dry wt. of matrix	36.05	30.38	29.24	27.78
$\frac{\text{conc. of water}}{\text{conc. of counterion}} \left(\frac{c_3}{c_1}\right)$	16.50	13.88	13.36	12.69
t_2^3	0.631	0.512	0.502	0.508
$\frac{c_3}{c_1} t_2^3$	10.41	7.11	6.71	6.45
t_3(obs)	9.41	6.63	12.85	11.36

The values for the observed t_3 values have been corrected for partial molal volume changes as described in Appendix A.6(Reference 87).

The t_2^3 values, the transport number of the co-ion in the corresponding binary solution.

$$J_s = \frac{l_{22}}{z_1^2} X_{12} + \left(\frac{-z_2 l_{23}}{z_1} \right) X_3 \qquad (6.30)$$

$$J_3 = \left(\frac{-z_2 l_{23}}{z_1} \right) X_{12} + (l_{33} - t_3^2 \alpha) X_3 \qquad (6.31)$$

Salt flows, J_s, and water flows, J_3, calculated by the S.M.C. are both lower than observed (table 6.4). The lower value of J_3 (eqn 6.31) is due primarily to the overestimation of t_3 in the dominant second term of that equation. Salt flow, J_s, is underestimated because the mobility coefficient l_{22} is underestimated by the Salt Model.

Investigation of the predictive capabilities of the S.M.C. was extended by determining experimentally the transference number of water, t_3, in C60N membranes which had been equilibrated in turn with equimolar (0.1M) solutions of HCl and of each of the alkali earth metal chlorides shown(table 6.5). The membranes were converted to their various forms as described in section 3.4, and the t_3 values determined as described in section 3.14. Observed and calculated values of t_3 are shown in table 6.5. It is seen that agreement is remarkably good for all forms except the Rubidium and the Caesium whose observed t_3 values are anomalously high.

CHAPTER 7

MIXED IONIC FORMS OF THE C60 SYSTEM

Introduction:

When a cation exchanger is placed in a solution containing a mixture of the electrolytes calcium chloride and sodium chloride an equilibrium is quickly set up at the solution-membrane interface so that

$$Ca^{2+} + 2\bar{Na}^{+} \rightleftharpoons \bar{Ca}^{2+} + 2Na^{+}$$

where the barred and unbarred symbols represent the membrane and solution phases respectively. The position of this equilibrium determines the selectivity for the two cationic species. This selectivity is usually measured in terms of a selectivity coefficient

$$K_{Na^+}^{Ca^{2+}},$$

$$K_{Na^+}^{Ca^{2+}} = \frac{\bar{X}_{Ca^{2+}} \; (a_{Na^+})^2}{(\bar{X}_{Na^+})^2 \; a_{Ca^{2+}}} \qquad (7.1)$$

The terms $\bar{X}_{Ca^{2+}}$ and $\bar{X}_{Na^+}$ are defined here as mole fractions of the ions in the exchanger and it may be shown that the relative amounts of Ca^{2+} and Na^+ in the exchanger depend on the total concentration of Ca^{2+} and Na^+ in the solution as well as on their relative concentrations. At low electrolyte concentrations approximations may be made to obtain the following relationship (109), where m is the total molality of Na^+ and Ca^{2+} in solution and X_{Na^+} and $X_{Ca^{2+}}$ are the mole fractions of Na^+ and Ca^{2+} in the solution phase,

$$K_{Na^+}^{Ca^{2+}} = \frac{\bar{X}_{Ca^{2+}}}{(\bar{X}_{Na^+})^2} \cdot \frac{m(X_{Na^+})^2}{X_{Ca^{2+}}} \qquad (7.2)$$

Alternatively eqn 7.2 may be arranged to consider the properties

of /

of the exchanger and the equilibrium solution separately i.e.,

$$\frac{(\bar{X}_{Na^+})^2}{\bar{X}_{Ca^{2+}}} \cdot K_{Na^+}^{Ca^{2+}} = \frac{m(X_{Na^+})^2}{X_{Ca^{2+}}} \qquad (7.3)$$

It is obvious that in order to maintain the left hand side of the expression constant neither the ratio $(X_{Na^+})^2 / X_{Ca^{2+}}$ nor the total molality of Na^+ and Ca^{2+} must be allowed to vary. This behaviour contrasts with the exchange between two species of univalent ions (107) where the ionic composition of the exchanger depends only on the relative concentrations of the ions in the solution phase and not on the total concentration.

$K_{Na^+}^{Ca^{2+}}$ is not a true equilibrium constant. A rational equilibrium constant $\mathcal{K}_{Na^+}^{Ca^{2+}}$ may be written however using the convention that the standard and reference states of the exchanger phase be defined as the respective ionic forms in equilibrium with pure water. The membrane phase activity coefficients are $\bar{\gamma}_{Ca^{2+}}$ and $\bar{\gamma}_{Na^+}$ so that

$$K_{Na^+}^{Ca^{2+}} = \frac{\bar{X}_{Ca^{2+}}}{(\bar{X}_{Na^+})^2} \cdot \frac{\bar{\gamma}_{Ca^{2+}}}{(\bar{\gamma}_{Na^+})^2} \cdot \frac{m(X_{Na^+})^2}{X_{Ca^{2+}}} \qquad (7.4)$$

Since $\mathcal{K}_{Na^+}^{Ca^{2+}}$ is defined to be constant the ratio $\bar{\gamma}_{Ca^{2+}} / (\bar{\gamma}_{Na^+})^2$ contains the variation of $K_{Na^+}^{Ca^{2+}}$ with composition.

Selectivity coefficients may be related to the appropriate free energy changes occurring when ions are exchanged. One such relation is

$$\Delta G^o = - RT \ln \mathcal{K}_{Na^+}^{Ca^{2+}} \qquad (7.5)$$

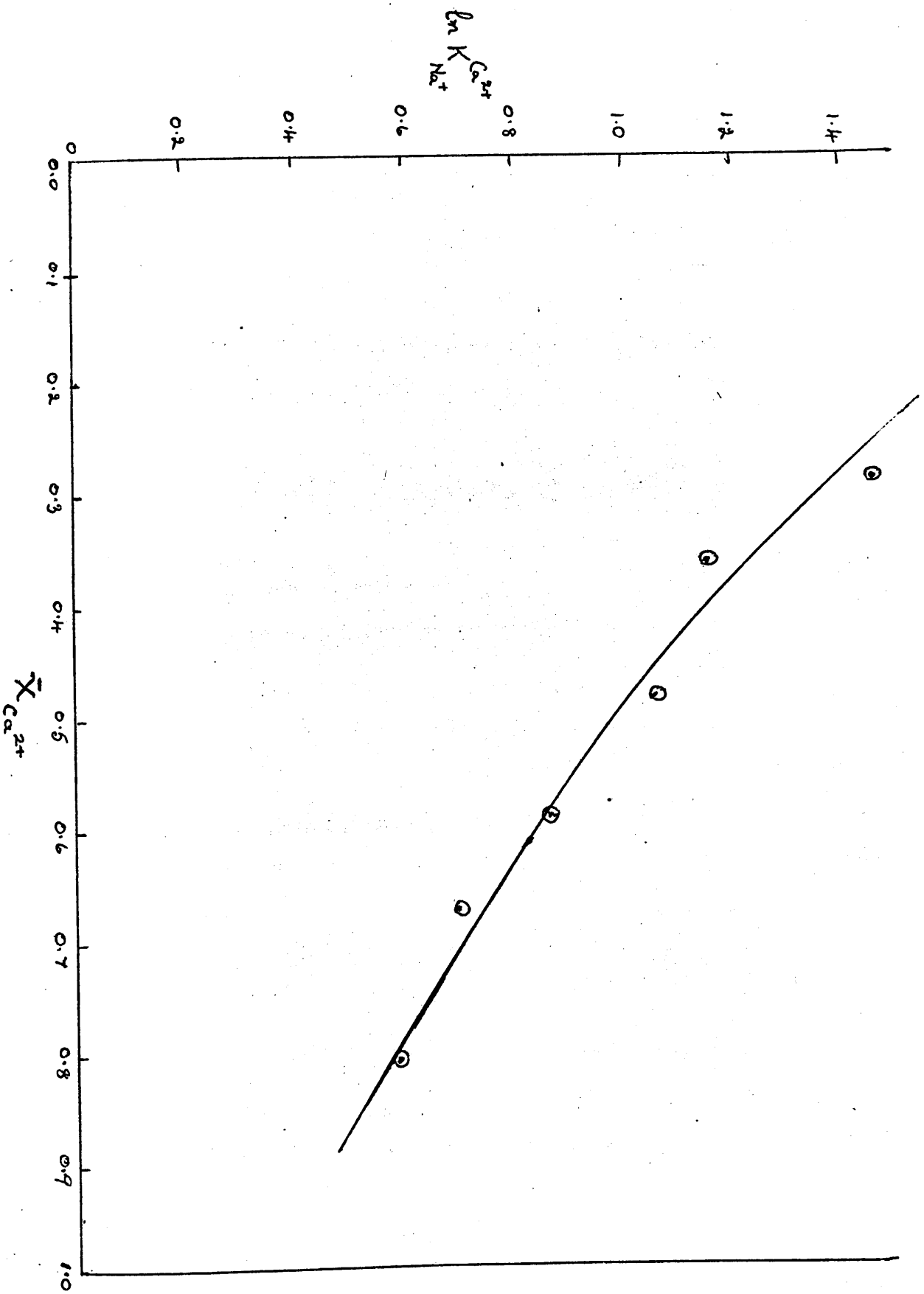
where G^o is the standard free energy change involved in the transfer of one mole of calcium from an infinite amount of solution in the conventional standard state to one mole of exchanger initially completely in the sodium form and the transfer back to the solution of /

Table 7.1

χ_{Na^+}	$\chi_{Ca^{2+}}$	$\ln K_{Na^+}^{Ca^{2+}}$	molality (m)	$\bar{\chi}_{Ca^{2+}}$
1	0	-	0.1	0
0.987	0.013	1.478	0.0988	0.295
0.974	0.026	1.150	0.0975	0.362
0.948	0.052	1.082	0.0950	0.482
0.888	0.112	0.863	0.0900	0.600
0.823	0.177	0.697	0.0850	0.671
0.600	0.400	0.576	0.0750	0.823

χ_{Na} and χ_{Ca} are the mole fractions of sodium and calcium ion respectively in the equilibrium solution. $\bar{\chi}_{Ca}$ is the mole fraction of calcium ion in the exchanger.

Figure 7.1


$\ln K^{Ca^{2+}}_{Na^+}$
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
$\bar{X}_{Ca^{2+}}$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

of one mole of sodium (i.e. the standard free energy involved in the complete conversion of one mole of the exchanger from the sodium form to the calcium form).

A completely general thermodynamic treatment using rational activities in the membrane phase has been given by Gaines and Thomas (108). Making use of the observations that co-ion uptake is negligible and the water activity in the solution remains essentially constant over the range $0 \leq \bar{X}_{Ca^{2+}} \leq 1$ at an overall ionic strength of 0.1 Normal, the general equation given by these authors may be reduced to,

$$\ln \mathcal{K}_{Na^+}^{Ca^{2+}} = (N^w_{Ca^{2+}} - N^w_{Na^+}) \ln a_w + \int_0^1 \ln K_{Na^+}^{Ca^{2+}} \, d\bar{X}_{Ca^{2+}} \qquad (7.6)$$

where $N^w_{Ca^{2+}}$ and $N^w_{Na^+}$ are the number of moles per equivalent of fixed ionic groups in the pure calcium and sodium forms respectively. A fuller description of quantitative theories of selectivity is given by Helfferich (2) Reichenberg (109) and Holm (110).

7.1 Selectivity Coefficient: A selectivity coefficient $K_{Na^+}^{Ca^{2+}}$ was calculated as described above for each equilibrium situation. The results obtained were tabulated (table 7.1) and a graph was plotted with $\ln K_{Na^+}^{Ca^{2+}}$ as a function of $\bar{X}_{Ca^{2+}}$ (figure 7.1).

To determine the rational equilibrium constant $\mathcal{K}_{Na^+}^{Ca^{2+}}$ of eqn 7.6 the values of $\ln K_{Na^+}^{Ca^{2+}}$ were fitted to a polynomial of the type $y = a + b\bar{X}_{Ca^{2+}} + c\bar{X}^2_{Ca^{2+}}$ by a least squares fitting procedure and the function integrated between the limits 0 and 1. A final value for $\mathcal{K}_{Na^+}^{Ca^{2+}}$ of 2.88 molal was obtained and may be used to calculate the standard free energy change of the ion exchange process from eqn 7.5

$$\Delta G^o = -RT \ln \mathcal{K}_{Na^+}^{Ca^{2+}} \qquad (7.5)$$

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The negative value (eqn 7.5) obtained for ΔG^{o} means that the calcium form is more stable than the sodium by 2622 joules. The graph of $\ln K_{Na}^{Ca^{2+}}$ against $\bar{X}_{Ca^{2+}}$ shows, as expected, that in the absence of pressure-volume effects $K_{Na}^{Ca^{2+}}$ decreases steadily as the mole fraction of calcium in the exchanger increases.

Bonner has indicated (111) that if exchanges between univalent and divalent ions or between two divalent ions are represented by equations of the type

$$\tfrac{1}{2}MX_2 + BRes = \tfrac{1}{2}MRes_2 + BX$$

and

$$\tfrac{1}{2}MX_2 + \tfrac{1}{2}QRes_2 = \tfrac{1}{2}MRes_2 + \tfrac{1}{2}QX_2$$

they are directly comparable with exchanges between univalent ions which are represented by the equation

$$AX + BRes = ARes + BX$$

When exchange reactions are represented in terms of equilibrium constants triangular comparisons may be obtained by addition or subtraction of two such equations to yield a third and the resultant equilibrium constant for the third reaction will be the product or quotient of the first two constants. This logarithmic additivity of equilibrium constants also permits the establishment of quantitative selectivity scales (112). Such selectivity scales for divalent ions are quoted by Bonner and Smith (113). These are based on the arbitrary assignment of the value of unity to the affinity of the lithium ion for each resin and provide a means of predicting a selectivity coefficient $K_{Na^+}^{Ca^{2+}}$ since

$$K_{Na^+}^{Ca^{2+}} = K_{Li^+}^{Ca^{2+}} K_{Na^+}^{Li^+}$$

From the selectivity scales of the above reference $K_{Li^+}^{Ca^{2+}}$ and $K_{Li^+}^{Na^+}$ are 4.15 and 1.58 respectively, so value of 2.63 may be predicted for /

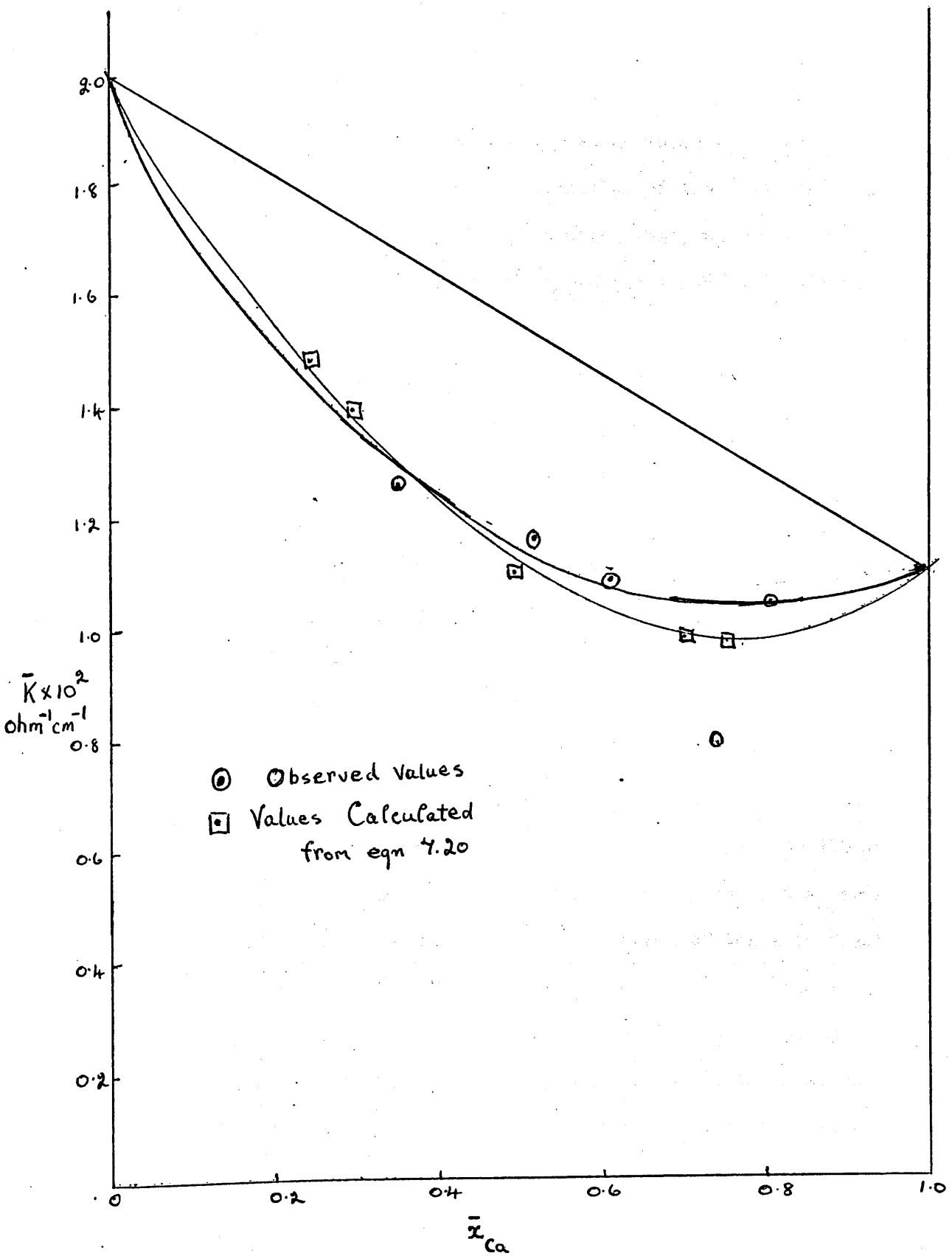
TABLE 7.2

χ_{Na^+}	$\chi_{Ca^{2+}}$	$\bar{x}_{Na^+}$	$\bar{x}_{Ca^{2+}}$	observed specific conductivity ($\bar{K}$) $(ohm^{-1}cm^{-1})x10^2$
1	0	1	0	1.99
0.987	0.013	0.640	0.360	1.26
0.974	0.026	0.468	0.532	1.20
0.948	0.052	0.352	0.648	1.12
0.888	0.112	0.250	0.750	0.69
0.823	0.177	0.194	0.806	1.04
0	1	0	1	1.10

χ represents the mole fraction of ions in equilibrium solution.

$\bar{x}$ represents equivalent fraction of ions in the membrane.

Figure 7.2


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
$\bar{K} \times 10^2$
ohm^{-1}cm^{-1}
$\bar{x}_{Ca}$
Observed Values
Values Calculated from eqn 4.20

for $K^{Ca^{2+}}_{Na^{+}}$ which is in general agreement with the observed.

7.2 Electrical Properties of Mixed Ionic Forms: The specific conductivity of the membrane was measured at each equilibrium stage (table 7.2) and a graph was drawn in which the specific conductivity ($\bar{K}$) was plotted as a function of the equivalent fraction of calcium ($\bar{x}_{Ca^{2+}}$) (figure 7.2). It was noted that, whilst the overall trend of $\bar{K}$ values is downwards as $\bar{x}_{Ca^{2+}}$ increases from zero to unity, a minimum value of $\bar{K}$ was obtained in the region $\bar{x}_{Ca^{2+}} = 0.5$. Despite the presence of the more mobile sodium ions in the membrane the net contribution of the two cationic species to the specific conductivity would appear to be negative over the observed $\bar{x}_{Ca^{2+}}$ range.

It was decided therefore to investigate this phenomenon using analogous ternary solutions data. No appropriate transport data was available for $NaCl-CaCl_2$ solutions. However, in view of the close similarity between the transport properties of calcium chloride and barium chloride solutions over the required concentrations (22)(86) it was decided that a meaningful comparison could be made between an alkali metal ion chloride-barium chloride solution data and the corresponding results from the membrane studies. Reference 115 in which the experimental specific conductivity values of the ternary solution $KCl-BaCl_2$ are displayed as a function of the mole fraction of barium shows that the conductivity values deviate slightly from the ideal. It is seen however that the function has no minimum and so is never less than the specific conductivity of the less mobile ion. The contribution of the more mobile ion to the specific conductivity of the solution is positive.

If the analogy of the ternary solution is however extended to the membrane system it consists of the calcium ions (α) and the sodium /

sodium ion (β), the matrix-fixed sulphonate ion (4), and the neutral solvent water (3). (It is assumed that the co-ion concentration is low enough to be negligible since its maximum concentration is 2% of the concentration (table 4.1)). As in the solution case the frame of reference is solvent-fixed and so the phenomenological equation matrix may be expressed as,

$$\begin{vmatrix} J_\alpha^3 \\ J_\beta^3 \\ J_4^3 \end{vmatrix} = \begin{vmatrix} L_{\alpha\alpha}^3 & L_{\alpha\beta}^3 & L_{\alpha 4}^3 \\ L_{\beta\alpha}^3 & L_{\beta\beta}^3 & L_{\beta 4}^3 \\ L_{4\alpha}^3 & L_{4\beta}^3 & L_{44}^3 \end{vmatrix} \begin{vmatrix} X_\alpha \\ X_\beta \\ X_4 \end{vmatrix} \qquad (7.7)$$

Current density I is given by

$$I = F(Z_\alpha J_\alpha^3 + Z_\beta J_\beta^3 + Z_4 J_4^3) \qquad (7.8)$$

where Z_i is the valency of ion i and F is a faraday.

Since in the system described there is no chemical potential gradient

$$X_i = Z_i F \left(- \frac{d\psi}{dx} \right) \qquad (2.13)$$

From equations 7.12 and 2.13

$$I = F^2 (Z_\alpha^2 L_{\alpha\alpha}^3 + Z_\beta^2 L_{\beta\beta}^3 + Z_4^2 L_{44}^3 + 2Z_\alpha Z_\beta L_{\alpha\beta}^3 + 2Z_\alpha Z_4 L_{\alpha 4}^3 + 2Z_\beta Z_4 L_{\beta 4}^3)(- \frac{d\psi}{dx}) \qquad (7.9)$$

Application of Ohm's Law (eqn 2.26) to this equation (7.9) yields the specific conductivity $\overline{K}$

$$\overline{K} = F^2 (Z_\alpha^2 L_{\alpha\alpha}^3 + Z_\beta^2 L_{\beta\beta}^3 + Z_4^2 L_{44}^3 + 2Z_\alpha Z_\beta L_{\alpha\beta}^3 + 2Z_\alpha Z_4 L_{\alpha 4}^3 + 2Z_\beta Z_4 L_{\beta 4}^3) \qquad (7.10)$$

It is noted that in the ternary description (eqn 7.10) the direct coefficients $L_{\alpha\alpha}^3$ and $L_{\beta\beta}^3$ both correspond to L_{11}^3 in the binary situations (43) and (section 2.4.1.1.), and the cross-coefficients /

coefficients $L^3_{\alpha 4}$ and $L^3_{\beta 4}$ correspond to L^3_{12} in the binary situations. Ternary cation-cation coupling coefficient $L^3_{\alpha\beta}$ has no binary analogue.

A set of equations similar to Miller's successful LN approximation (114) may be formulated,

$$L^3_{11} = \bar{x}_i (L_{11})_i \text{(where } i = \alpha, \beta) \quad (7.11)$$

$$L^3_{44} = \bar{x}_\alpha (L_{44})_\alpha + \bar{x}_\beta (L_{44})_\beta \quad (7.12)$$

$$L^3_{i4} = \bar{x}_i (L_{i4})_i \qquad (i = \alpha\ \beta) \quad (7.13)$$

$$-L^3_{\alpha\beta} = (\bar{x}_\alpha\ \bar{x}_\beta)^{3/2} \quad (L_{\alpha 4})(L_{\ 4})^{\frac{1}{2}} \quad (7.14)$$

By substituting equations 7.11 - 7.14 into equation 7.10 the expression

$$\bar{K} = F^2(Z^2_\alpha \bar{x}_\alpha (L_{11})_\alpha + Z^2_\beta \bar{x}_\beta (L_{11})_\beta + Z_4 Z_\alpha \bar{x}_\alpha (L_{44})_\alpha + Z^2_4 \bar{x}_\beta (L_{44})_\beta$$

$$+ 2Z_\alpha Z_\beta (L_{\alpha\beta}) + 2Z_\alpha Z_4 \bar{x}_\alpha (L_{14})_\alpha + 2Z_\beta Z_4 \bar{x}_\beta (L_{14})_\beta) \quad (7.15)$$

is obtained ($)_\alpha$ and ($)_\beta$ denote the calcium and sodium forms respectively of the corresponding binary. $\bar{x}_i$ is the equivalent fraction of species i.

For the calcium binary solution,

$$\bar{K} = (Z^2_\alpha (L_{11})_\alpha + Z^2_4 (L_{44})_\alpha + 2Z_\alpha Z_4 (L_{\alpha 4})_\alpha) F^2 \quad (7.16)$$

and in sodium binary,

$$\bar{K} = (Z^2_\beta (L_{11})_\beta + Z^2_4 (L_{44})_\beta + 2Z_\beta Z_4 (L_{\beta 4})_\beta) F^2 \quad (7.17)$$

Equation 7.15 therefore becomes,

$$\bar{K} = (\bar{x}_\alpha K_\alpha + \bar{x}_\beta K_\beta + (2Z_\alpha Z_\beta (L_{\alpha\beta})) F^2 \quad (7.18)$$

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TABLE 7.3

$\bar{x}_{Na}$	$\bar{x}_{Ca}$	Correction term (calculated)$\times 10^2$	Calculated specific conductivity $\bar{K}$ ohm^{-1} cm^{-1} $\times 10^2$
1.00	0.00	0.00	1.99
0.75	0.25	-0.26	1.49
0.70	0.30	-0.30	1.40
0.50	0.50	-0.39	1.11
0.30	0.70	-0.30	1.00
0.25	0.75	-0.26	0.99
0.00	1.00	0.00	1.10

The ideal situation,

$$\overline{K} = (\bar{x}_\alpha \overline{K}_\alpha + \bar{x}_\beta \overline{K}_\beta)\ F^2 \qquad (7.19)$$

would obviously give a linear relationship. The final term however, the cation-cation coupling interaction, is shown in eqn. 7.14 to be negative and would reduce the specific conductivity from the maximum value of the ideal situation. (figure 7.2).

Table 7.3 shows values for the correction term T calculated from eqn. 7.20 using mobility l_{ik}- coefficients which have been converted from a membrane-fixed frame of reference (l_{ik}) to a solvent-fixed frame of reference (L_{ik}) (Appendix A.7).

$$\text{Correction Term (T)} = -2Z_\alpha Z_\beta (\bar{x}_\alpha \bar{x}_\beta)^{3/2}\ ((L_{\alpha 4})\ (L_{\beta 4})\ )^{\frac{1}{2}} \qquad (7.20)$$

calculated over the concentration range $0 \leqslant \bar{x}_\alpha \leqslant 1$. In the calculation of the term (T) in eqn. 7.20 no correction has been included to account for the change in path tortuosity of the membrane during its transition from the sodium form to calcium because it was found to be negligible in this context.

It is evident that both calculated and observed specific conductivity functions show a minimum value.

Table 7.4

$\bar{x}_{Ca^{2+}}$	meq. Ca^{2+}	meq. H_2O	$\frac{\Delta \text{meq. } H_2O}{\Delta \text{meq. Ca}}$
0	0	8.00	-
0.360	0.090	7.50	-5.56
0.532	0.134	7.23	-6.13
0.648	0.163	7.05	-6.21
0.750	0.188	6.89	-6.40
0.806	0.202	6.78	-7.85
1	0.251	6.49	-12.08

7.3 Results and discussion:

Swelling Pressure: It is seen in (table 7.4) that the water content of the membrane decreases with increasing concentration of calcium in the membrane. Therefore, the swelling pressure exerted on the membrane (section 4.11) decreases with increasing calcium content. By correlating each measured water content with the corresponding calcium ion concentration in the membrane it is possible to calculate the average number of water molecules which leave the membrane when a sodium ion is displaced by a calcium ion. The results of these studies are shown in table 7.1. It is noted (table 7.4) that the rate Δ m.eq H_2O /Δ m.eq Ca^{2+} increases only slightly until the equivalent fraction of calcium in the membrane rises to about 0.75. A more rapid increase is then recorded.

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APPENDIX A.1

E.M.F. OF A CONCENTRATION CELL AND CALCULATION OF X_1 AND X_2

a) E.M.F. of a Concentration cell

In a cell such as that represented by figure A.1.1, where an ion exchange membrane separates two aqueous solutions of the same 2:1 electrolyte on sides ' and " respectively, salt and water flows occur in opposite directions and a diffusion potential is set up. If the assumption is made that there is no interfacial resistance at the membrane surface then the potential, E, measured between the electrodes is given by,

$$E = E_1 + E_m + E_2 \qquad (A.1.1)$$

The membrane will be chosen to be a cation exchanger and the electrodes reversible to the co-ion so that,

$$E_1 = \frac{RT}{Z_2F} \ln a_2' \qquad (A.1.2a)$$

$$E_2 = \frac{RT}{Z_2F} \ln \frac{1}{a_2''} \qquad (A.1.2b)$$

The diffusion potential, E_m, is given by the integral of equation 2.37 across the entire membrane,

$$E_m = \frac{RT}{F} \left\{ \frac{t_1}{Z_1} \ln\left(\frac{a_1''}{a_1'}\right) + \frac{t_2}{Z_2} \ln\left(\frac{a_2''}{a_2'}\right) + t_3 \ln\left\{\left(\frac{a_3''}{a_3'}\right)\right\}\right\} \qquad (A.1.3)$$

Strictly speaking, t_1, t_2 and t_3 in equation A.1.3 are the mean values of the transport and water transference numbers of the membrane over the concentration interval $a_i' - a_i''$ $(i=1,2,3)$, but providing the concentration gradients are small the variation in t_i across the membrane should be negligible.

Substituting/

Substituting $t_2 = 1-t_1$, $Z_1 = 2$, $Z_2 = -1$ and rearranging, equation A.1.3 becomes,

$$E_m = \frac{RT}{F}\left\{\frac{t_1}{2}\ln\left\{\left(\frac{a''_1}{a'_1}\right)\left(\frac{a''_2}{a'_2}\right)^2\right\} + t_3\ln\left\{\left(\frac{a''_3}{a'_3}\right) - \ln\left(\frac{a''_2}{a'_2}\right)\right\}\right\} \qquad (A.1.4)$$

and since $a''_1.(a''_2)^2 = (a''_{\pm})^3$ and $a'_1.(a'_2)^2 = (a'_{\pm})^3$ the equation may be rewritten,

$$E_m = \frac{RT}{F}\left\{\frac{3}{2}t_1\ln\left(\frac{a''_{\pm}}{a'_{\pm}}\right) + t_3\ln\left(\frac{a''_3}{a'_3}\right) - \ln\left(\frac{a''_2}{a'_2}\right)\right\} \qquad (A.1.5)$$

The total cell potential, E, given by equation A.1.1 is therefore

$$E = \frac{3RT}{2F}t_1\ln\left(\frac{a''_{\pm}}{a'_{\pm}}\right) + \frac{RT}{F}t_3\ln\left(\frac{a''_3}{a'_3}\right) \qquad (A.1.6)$$

b) Calculation of X_1 and X_2

The electrochemical potential of the salt, u_{12}, is defined as

$$u_{12} = r_1u_1 + r_2u_2 \qquad (A.1.7)$$

where u_1 and u_2 are the electrochemical potentials of cation and anion respectively, and r_1 and r_2 are the stoichiometric constants. If u_1 and u_2 are separated into chemical and electrical components then,

$$u_{12} = r_1u_1 + r_2u_2 + (r_1Z_1 + r_2Z_2)F\psi = r_1u_1 + r_2u_2 \qquad (A.1.8)$$

i.e. the chemical and electrochemical potentials of the salt are identical. This identity can be used to calculate X_1 and X_2 since,

$$\left(\frac{du_{12}}{dx}\right) = r_1\left(\frac{du_1}{dx}\right) + r_2\left(\frac{du_2}{dx}\right) = r_1X_1 + r_2X_2 = \left(\frac{du_{12}}{dx}\right) \qquad (A.1.9)$$

Equation A.1.9 in conjunction with equation 2.37 which may be written

$$\frac{t_1}{Z_1}X_1 /$$

$$\frac{t_1}{Z_1} X_1 + \frac{t_2}{Z_2} X_2 + t_3 \ln \left(\frac{a_3''}{a_3'} \right) = 0 \qquad (2.37)$$

leaves X_1 and X_2 as the only unknowns and the equations may therefore be solved for these quantities.

APPENDIX A.2

RADIOCHEMICAL DETERMINATION OF UPTAKES

There are two possible approaches to this. The first is to measure the activity of a known volume of radioactive solution before and after placing an inactive membrane into it. The alternative is to equilibrate a membrane in active solution, remove it and place it in a known volume of inactive solution and measure the increase of activity in this solution. For reasons which will be discussed below this second method was employed for both selectivity and coion uptake measurements.

Consider a membrane containing B milliequivalents of ion X. If this is placed in equilibrium solution containing radioactive X ions an isotopic exchange will occur until the isotopic compositions of X ions in the solution and in the membrane are identical. Samples of the solution will give the counts per minute per milliequivalent of X ions in the solution and hence the membrane (=y).

If the membrane is then blotted and freed from adhering solution films as described in section 3.8, then the total counts per minute in the membrane phase will be B x y. The membrane is then placed in a known volume of an identical inactive solution containing A milliequivalents of X ions.

Total X ion in the system is thus A+B milliequivalents. Isotopic redistribution occurs and the total activity appearing in the solution is A/(A+B) x B x y. This activity can be determined by taking samples of the solution after equilibration which leaves B as the only unknown.

By an exactly analogous procedure the expression for the total activity in the solution using the first method is A/(A+B) x A x y. This method is only suitable where a large reduction in solution counts

can/

can be expected, which means that A and B must be at least of the same order with preferably $B \gg A$. Measurement of coion uptakes, where $A \gg B$, is clearly grossly inaccurate by this method and in selectivity measurements even although in some cases A was slightly larger than B, this first method resulted in the subtraction of two large numbers with consequent inaccurate results. The second method was therefore used in all determinations.

APPENDIX A.3

EFFECT OF SAMPLING ON MEASURED TRACER FLOWS

Consider a half-cell of volume vo into which tracer ions are diffusing at an instantaneous rate of inc, where inc is some function of time. If the half-cell is sampled to determine the activities at given times, then volume changes and/or dilution effects will result, giving an incorrect plot of activity against time. Ideally it is desired to sample without disturbing the system so that a correct plot is obtained. The undisturbed system will therefore be taken as a reference. In the general derivation below the deviation from this ideality due to any form of sampling is calculated.

Let the volume of the sample removed be nn and let a be the volume of inactive solution added. (This means that the sample removed can be as large as necessary without ultimately causing a potentially catastrophic reduction in the volume of the sampling side).

Consider firstly the $i-1^{th}$ sample.

Activity/sample = $y[i-1]$

Volume when $i-1^{th}$ sample is taken = $vo - (i-2)(nn-a)$.

Time at which sample is taken = $x[i-1]$.

Volume after sample is removed = $vo - (i-1)(nn-a) - a$.

Total activity remaining = $y[i-1](vo - (i-1)(nn-a) - a)/nn$.

Volume a of inactive solution is added, therefore the volume of the system now becomes $vo - (i-1)(nn-a)$.

The i^{th} sample is taken at time $x[i]$.

Between $x[i-1]$ and $x[i]$, tracer has been diffusing into the half-cell and the total activity added during this time interval is

$$\frac{vo}{nn}\int_{x[i-1]}^{x[i]} inc[i]\,dx$$

Note/

Note that the units of inc[i] are activity/ unit time/ ml. (referred to the standard volume vo)/ sample.

Therefore at time x[i] the activity/ sample is,

$$\frac{y[i-1](vo - (i-1)(nn-a) - a) + vo \int_{x[i-1]}^{x[i]} inc[i]\,dx}{vo - (i-1)(nn-a)} = y[i]$$

Rearranging,

$$\int_{x[i-1]}^{x[i]} inc[i]\,dx = \frac{((y[i] - y[i-1](vo - (i-1)(nn-a)) + y[i-1])}{vo}$$

In the steady state inc[i] is a constant and therefore,

$$inc\ i = \frac{((y[i] - y[i-1])(vo - (i-1)(nn-a)) + ay[i-1])}{vo\ (x[i] - x[i-1])}$$

so that the mean value of the inc[i] may be calculated for a given run for time intervals x[i] - x[i-1].

In the non-steady state, inc[i] is a function of time and $\int_{x[i-1]}^{x[i]} inc[i]\,dx$ gives the total increase in activity for one time interval (referred to the standard volume vo) without any information on the rate inc[i].

Returning to the equation for y[i] then,

$$y[i] = y[i-1] + \frac{(vo \int_{x[i-1]}^{x[i]} inc[i]\,dx - a\,y[i-1])}{(vo - (i-1)(nn-a)}$$

Expanding the numerator vo to vo - (i-1)(nn-a) + (i-1)(nn-a), and collecting terms,

y i /

$$y[i] = y[i-1] + \int_{x[i-1]}^{x[i]} inc[i]dx$$

$$+ \frac{(i-1)(nn-a)\int_{x[i-1]}^{x[i]} inc[i]dx - ay[i-1]}{vo - (i-1)(nn-a)}$$

As mentioned at the beginning, it is necessary to refer all activities to the undisturbed system, therefore,

$y[i-1] = y[i-1]_{vo} - corr[i-1]$, where the subscript vo refers to the unperturbed activity and the difference is made up by the term $corr[i-1]$.

Therefore,

$$y[i]_{vo} - corr[i] = y[i-1]_{vo} + \int inc[i]dx$$

$$y[i]_{vo} - corr[i] = y[i-1]_{vo} + \int inc[i]dx + \frac{(i-1)(nn-a)\int inc[i]dx - ay[i-1]}{vo - (i-1)(nn-a)} - corr[i-1]$$

In the ideal case,

$$y[i]_{vo} = y[i-1]_{vo} + inc[i]dx$$

thus,

$$corr[i] = \frac{ay[i-1] - (i-1)(nn-a)\int inc[i]dx}{vo - (i-1)(nn-a)} + corr[i-1]$$

and corr 1 = 0.0.

In this form the expression appears in the steady and non-steady state diffusion programs (Appendix A.9).

The true curve is obtained by plotting the $y[i]_{vo}$ against time $x[i]$.

APPENDIX A.4

FILM DIFFUSION CORRECTIONS

In the derivation of the expression for the self-diffusion coefficient $\bar{D}_A$ it was assumed that diffusion through the membrane was the rate-controlling step and that there was no interfacial resistance to diffusion between the membrane and the solution. In a real system however neither assmption is strictly true. The interfacial resistance problem, from which the difficulties arise, has been circumvented by the invention of the "diffusion layer" concept; i.e. that there exists at both membrane faces a layer of average thickness δ which unstirred regardless of the efficiency of stirring in the bulk solution. If diffusion through the membrane is faster than through the unstirred films then a concentration gradient is set up in the unstirred layers and this gradient lowers the measured diffusion coefficient. By this device the assumption of no interfacial resistance is preserved and all effects are ascribed to the diffusion layer. If the fluxes through the unstirred films and the membrane are equated it can be easily shown that for a mobile species, i, (1)

$$J_i = \frac{-\bar{D}_i \bar{c}_i}{d\left(1 + \frac{2\bar{D}_i \bar{c}_i \delta}{D_i c_i d}\right)} \qquad (A.4.1)$$

and hence,

$$\bar{D}_{iA} = \frac{\bar{D}_i}{\left(1 + \frac{2\bar{D}_i \bar{c}_i \delta}{D_i c_i d}\right)} \qquad (A.4.2)$$

where/

where D_i and c_i are the diffusion coefficient and concentration of i in the solution phase.

If $\frac{D_i c_i d}{\bar{D}_i \bar{c}_i \delta} \gg 2$, which is frequently the case for co-ions and water, then the diffusion process is membrane controlled. If, on the other hand, $\frac{D_i c_i d}{\bar{D}_i \bar{c}_i \delta} \ll 2$, then the rate-controlling step is diffusion through the films. Counterion diffusion usually lies somewhere between the two extremes so that the observed and true membrane diffusion coefficients ($\bar{D}_{1A}$ and $\bar{D}_1$ respectively) may differ significantly. There have been several attempts to correct self-diffusion data for the effects of film diffusion or to calculate δ directly (2)(3)(4)(5)(6) but the correction applied to observed diffusion coefficients in this work was that of Scattergood and Lightfoot (7). These authors calculated the mean local mass transfer coefficient, k_c, in the boundary layers (where k_c corresponds to the term D_1/δ in equations A.4.1 and A.4.2 above).

An important factor in determining the magnitude of k_c is the cell and paddle system geometry and it is therefore necessary to calibrate the diffusion cell before taking measurements. This was done by making limiting current measurements with a silver foil cathode in place of the membrane and 0.0005 molar silver nitrate in 1.0 molar sodium nitrate. The current was drawn from an automatic polarograph which gave a linearly increasing voltage with time. A plot of current against time was obtained by monitoring the potential difference across a standard 10 ohm resistor in the circuit with a potentiometric/

potentiometric chart recorder. At currents below the limiting current a linearly increasing plot of current against time was obtained, but when the limiting current was reached the trace levelled off to give a plateau. The experiment was repeated a number of times at stirring speeds of 250, 300, 350, 400, 450, 500 and 550 r.p.m. Overall reproducibility of limiting currents was about 2-3%. The mass transfer coefficient, k_c, is related to the limiting current I by the equation,

$$k_c = \frac{I^{\infty}}{F (c_1)_b} \qquad (A.4.3)$$

where $(c_1)_b$ is the concentration of ion 1 in the bulk solution and the general relation between the mass transfer coefficients and the other variables in the system is,

$$\frac{(k_c)_m B}{D} = A (NL^2\rho/\eta)^q (\eta/\rho D)^{\frac{1}{3}} \qquad (A.4.4)$$

where $(k_c)_m$ is the area mean value of k_c,

B is the cathode diameter,

D is the solvent diffusivity,

N is the rate of impellar rotation,

L is the impellar diameter,

η is the solution viscosity,

ρ is the solution density

and A and q are the constants of the system to be determined.

If the logarithms of both sides of equation A.4.4 are taken, the equation may be rearranged to become,

$$\log \frac{(k_c)_m B}{D} = q \log N + \log \left(A (\eta/\rho D)^{\frac{1}{3}} (L^2\rho/\eta)^q \right) \qquad (A.4.5)$$

A/

A plot of log $\frac{(k_c)_m B}{D}$ versus log H should therefore be a straight line of gradient q. Substitution of q into the constant term yields A. A value for A of 0.26 and, for q, 0.50 were obtained for the cell employed in all self diffusion measurements in this study. Determination of these constants permits the evaluation of k_c for any other membrane and solution from equation A.4.4 and allows a correction for film diffusion effects to be applied.

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Appendix A.5

Correction to Transport Numbers for Uptake of Chlorine-36 by the Electrodes

In the experiments to determine the transport numbers of the co-ions in the membrane, Ag / AgCl electrodes were used in the solutions of calcium chloride containing Cl^{36}. In the back-flow experiments, i.e. with the flow of chloride^{36} against the electric current, the electrode in the solution containing a high activity of Cl^{36} was the anode, so that AgCl was being formed on the electrode and the total chloride concentration (and hence the Cl^{36} concentration) was being reduced. The duration of the experiment and the current density used were so adjusted that this concentration change was small, approx 2-3% of the total concentration. Since the Cl^{36} concentration was assumed constant in the calculation, an average value over the duration of the experiment was used without introducing any great error into the result. In the other side of the cell, chloride ions were being released into the solution, but since only the concentration of Cl^{36} ions permeating the membrane was being measured, the effect on the results was negligible. This was not the case when the forward flow was being measured. Here the anode was situated in the low activity solution and hence Cl^{36} ions were being removed from this solution with a consequent reduction in the counting rate of the samples removed for analysis. The apparent flow rate of Cl^{36} was therefore less than the true value. Since the rate of increase of the Cl^{36} concentration in the sampling side was constant as was the current density the number of Cl^{36} ions removed from the solution and consequently, the reduction in count rate could be obtained by the following method.

Consider a time t seconds after the start of the experiment.

The/

The total number of chloride ions removed from the solution on to the electrode in this time is

$$C_{Cl} = \frac{I\ t\ N_a}{F} \qquad (A.5.1)$$

where I is the total current in amps, F isa Faraday and N_a is Avogadro's number.

During this time an increasing number of these ions will have been Cl^{36} ions and this rate of increase will be constant. Thus the number of Cl^{36} ions removed from the solution can be expressed as follows:

$$C_{Cl} = \frac{N^*}{N^T} \cdot \frac{I\ t\ N_a}{F} \qquad (A.5.2)$$

where the value of $\frac{N^*}{N^T}$ is obtained as follows.

From the laws of radioactive decay,

$$k\ N^* = -\frac{dN^*}{dt} \qquad (A.5.3)$$

therefore,

$$N^* = (1/k)(-dN^*/dt) \qquad (A.5.4)$$

where k is the rate constant for the decay process and $(-dN^*/dt)$ is the rate of decay as measured by the counting rate of the samples. Also N^T is given by VcN_a, where V is the volume of the half cell and c the concentration of chloride ions in the solution.

Therefore equation (A.5.2) becomes,

$$\text{Number of } Cl^{36} \text{ ions removed from soln.} = C_{Cl} = \frac{(1/k)(-dN^*/dt)}{VcN_a} \cdot \frac{I\ t\ N_a}{F} \qquad (A.5.5)$$

$$= \frac{(1/k)(-dN^*/dt)\ I\ t}{VcF}$$

Tó/

To express this as a count rate equation (A.5.3) is used and the reduction in the counts produced during time t by the formation of $AgCl^{36}$ is,

$$\frac{k\,(\,1/k\,)(\,-dN^{*}/dt\,)\,I\,t}{VcF}$$

i.e. $$\frac{(\,-dN^{*}/dt\,)\,I\,t}{VcF}$$

This quantity must be added to each sample count rate in order to obtain the true activity in the solution at that time before calculation of the transport number is done.

APPENDIX A.6

Partial Molal Volume Calculations

The partial molal volume of an electrolyte $\bar{V}_{12}$ may be visualised by considering a reservoir of water so large that the addition of one mole of electrolyte will not alter the concentration. The change in volume of the water when one mole of electrolyte 1,2 is added to this large reservoir, of volumeV, is the partial molal volume of the electrolyte at the indicated concentration at constant temperature, T, pressure, P, and moles of the other components n. The partial molal volume can be represented by the partial derivatives of the total volume with respect to concentration at constant T,P, and n (n_3 = moles of water),

$$\bar{V}_{12} = \left(\frac{\delta V}{\delta n_{12}}\right)_{T,P,n} \qquad \text{A.6.1}$$

It can be shown that (1)

$$V = n_3\bar{V}_3 + n_{12}\bar{V}_{12} + \text{- - - - - - -} \quad \text{T,P constant} \qquad \text{A.6.2}$$

The partial molal volume of an electrolyte $\bar{V}_{12}$ may be evaluated from density measurements (2). For binary solutions the apparent molal volume Q_V is a more convenient method.

The apparent molal volume Q_V is defined by the relationship

$$Q_V = \frac{V - n_3\bar{V}_3^o}{n_{12}} \qquad \text{T,P constant} \qquad \text{A.6.3}$$

where V is the volume of the solution containing n_3 moles of water and n_{12} moles of electrolyte, and $\bar{V}_3^o$ is the molar volume of pure water at a given T and P ($\bar{V}_3^o = M_3/d^o$ where M_3 is the molecular weight of water and d^o is the density of water). Since $nV = n_{12}Q_V + n_3.\bar{V}_3^o$ the the partial molal volume of the electrolyte 1,2 and water 3 are given by the equation

$$\bar{V}_{12} = \left(\frac{\delta V}{\delta n_{12}}\right)_{T,P,n} = Q_V + n_{12}\left\{\frac{\delta Q_V}{\delta n_{12}}\right\}_{T,P,n} \qquad \text{A.6.4}$$

and /

$$\bar{V}_3 = \frac{V - n_{12}\bar{V}_{12}}{n_3} = \frac{1}{n_3}\left\{ n_3\bar{V}_3^{\circ} - n_{12}^2 \left(\frac{\partial Q_V}{\partial n_{12}}\right)\right\}_{T,P,n} \qquad \text{A.6.5}$$

The apparent molal volume may be expressed in terms of the measured density d and the molecular weight n_3 and M_{12} of the water and electrolyte so that

$$Q_V = \frac{1}{n_{12}}\left\{ \frac{n_3M_3 + n_{12}M_{12}}{d} - n_3\bar{V}_3^{\circ}\right\} \qquad \text{A.6.6}$$

On the molar concentration scale where $n_{12} = c$ the molarity equation A.6.6 becomes

$$Q_V = \frac{1000\ (d^{\circ} - d)}{cd^{\circ}} + \frac{M_{12}}{d^{\circ}} \qquad \text{A.6.7}$$

where d is the density of the solution

By using the relationship

$$c = \frac{md^{\circ}\ 1000}{1000 + Q_V md^{\circ}} \qquad \text{A.6.8}$$

the partial molal volume of electrolyte and water may be determined from the molarity concentration scale by the equations

$$\bar{V}_{12} = Q_V + \left\{ \frac{1000 - cQ_V}{2000 + c^{3/2}\left(\frac{\partial Q_V}{\partial\sqrt{c}}\right)}\right\} c^{\frac{1}{2}} \left\{ \frac{\partial Q_V}{\partial\sqrt{c}}\right\} \qquad \text{A.6.9}$$

and

$$\bar{V}_3 = \frac{2000\ \bar{V}_3^{\circ}\ (18.016\ /\ d^{\circ})}{2000 + c^{3/2}\left\{\frac{\partial Q_V}{\partial\sqrt{c}}\right\}} \qquad \text{A.6.10}$$

At infinite dilution the partial molal volume $\bar{V}_{12}^{\circ}$ and the apparent molal volume Q_V° are therefore equal.

Masson /

Table A.6.1

Electrolyte	Concentration (molar)	Q_v°	S_v^*
HCl	0.1	18.20	0.830
LiCl	0.1	17.00	1.488
CsCl	0.1	39.15	2.172
NaCl	0.1	16.40	2.153
RbCl	0.1	31.87	2.219
KCl	0.1	26.52	2.327

Q_v° and S_v^* are respectively the apparent molal volume at infinite dilution and the experimental slope of equation A.6.11.

The above data was collected from reference 6.

Masson (3) found that the apparent molal volumes of electrolytes Q_V vary with the square root of the molar concentration by the linear equation

$$Q_V = Q_V^o + S_V^* \sqrt{c} \qquad \text{A.6.11}$$

where S_V^* is the experimental slope ($S_V^* = \frac{\partial Q_V}{\partial \sqrt{c}}$) and that this simple relationship often extends to concentrated solutions. Scott (4) and Geffcken (5) have also examined this equation A.6.11 and found that it adequately represents the concentration dependence of Q_V over a wide temperature range (0 - 100°C).

The partial molal volumes of the electrolytes may therefore be determined from equation A.6.9 by firstly evaluating Q_V using equations A.6.11. The values of Q_V^o and S_V^* are tabulated (table A.6.1) (6) for the electrolytes investigated. It is noted that the volume change at the cathode caused by the passage of one coulomb of electricity is $\overline{V}_{Ag} - \overline{V}_{AgCl}$ (i.e. 10.27 -25.78 = -15.51) where $\overline{V}_{Ag}$ and $\overline{V}_{AgCl}$ are the partial molal volumes of silver and silver chloride respectively.

The partial molal volume of calcium chloride is therefore calculated using equations A.6.9 and A.6.11 to be 19.58 mls and the correction factor (β) is 0.32.

An alternative method of calculating the apparent molal volume values was also investigated. This method involved the use of the Redlick-Meyer equation (7) which is

$$Q_V = Q_V^o + S_V \sqrt{c} + b_V c \qquad \text{A.6.12}$$

where S_V is the theoretical limiting slope and b_V is an emperical constant determined from the experimental results. This equation A.6.12 produced a correction factor β of 0.30 for calcium chloride. The discrepency between the two methods was well within the experimental error quoted.

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APPENDIX A.7

SOLVENT FIXED MOBILITY COEFFICIENTS

Starting from equations 2.11

$$\phi = \sum_{i=1}^{4} J_i X_i \qquad (2.11)$$

and 2.14

$$\sum_{i=1}^{4} c_i X_i = 0 \qquad (2.14)$$

the latter equation can either be used to eliminate X_4 from equation 2.11 and so give the phenomenological equations appropriate to the membrane fixed frame of reference.

$$(J_1 - \frac{c_1}{c_4} J_4) = l_{11}X_1 + l_{12}X_2 + l_{13}X_3 \qquad (A.7.1a)$$

$$(J_2 - \frac{c_2}{c_4} J_4) = l_{21}X_1 + l_{22}X_2 + l_{23}X_3 \qquad (A.7.1b)$$

$$(J_3 - \frac{c_3}{c_4} J_4) = l_{31}X_1 + l_{32}X_2 + l_{33}X_3 \qquad (A.7.1c)$$

or alternatively eliminate X_3 and give the solvent-fixed phenomenological equations

$$(J_1 - \frac{c_1}{c_3} J_3) = L_{11}X_1 + L_{12}X_2 + L_{14}X_4 \qquad (A.7.2a)$$

$$(J_2 - \frac{c_2}{c_3} J_3) = L_{21}X_1 + L_{22}X_2 + L_{24}X_4 \qquad (A.7.2b)$$

$$(J_4 - \frac{c_4}{c_3} J_3) = L_{41}X_1 + L_{42}X_2 + L_{44}X_4 \qquad (A.7.2c)$$

If X_3 is eliminated from equations A.7.1a-c, using equation 2.14, and the/

the terms collected, they may be rewritten,

$$(J_1 - \frac{c_1}{c_4}J_4) = (l_{11} - \frac{c_1}{c_3}l_{13})X_1 + (l_{12} - \frac{c_2}{c_3}l_{13}) - \frac{c_4}{c_3}l_{13}X_4 \qquad \text{(A.7.3a)}$$

$$(J_2 - \frac{c_2}{c_4}J_4) = (l_{21} - \frac{c_1}{c_3}l_{23})X_1 + (l_{22} - \frac{c_2}{c_3}l_{23}) - \frac{c_4}{c_3}l_{23}X_4 \qquad \text{(A.7.3b)}$$

$$(J_3 - \frac{c_3}{c_4}J_4) = (l_{31} - \frac{c_1}{c_3}l_{33})X_1 + (l_{32} - \frac{c_2}{c_3}l_{33}) - \frac{c_4}{c_3}l_{33}X_4 \qquad \text{(A.7.3c)}$$

These equations may be made formally identical to equations A.7.2a-c by subtracting $\frac{c_1}{c_3}$ times eqn A.7.3c from eqn A.7.3a, subtracting $\frac{c_2}{c_3}$ times eqn A.7.3c from eqn A.7.3b and finally multiplying eqn A.7.3c all through by $-\frac{c_4}{c_3}$.

By equating coefficients in these resultant equations with those of eqns A.7.2a-c the following expressions for L- coefficients in terms of l- coefficients are obtained.

$$L_{11} = l_{11} - 2\frac{c_1}{c_3}l_{13} + \frac{c_1^2}{c_3^2}l_{33} \qquad \text{(A.7.4)}$$

$$L_{12} = l_{12} - \frac{c_2}{c_3}l_{13} - \frac{c_1}{c_3}l_{23} + \frac{c_1c_2}{c_3^2}l_{33} \qquad \text{(A.7.5)}$$

$$L_{22} = l_{22} - 2\frac{c_2}{c_3}l_{23} + \frac{c_2^2}{c_3^2}l_{33} \qquad \text{(A.7.6)}$$

$$L_{14} = \frac{c_1c_4}{c_3^2}l_{33} - \frac{c_4}{c_3}l_{13} \qquad \text{(A.7.7)}$$

$$L_{24} = \frac{c_2c_4}{c_3^2}l_{33} - \frac{c_4}{c_3}l_{23} \qquad \text{(A.7.8)}$$

$$L_{44} = \frac{c_4^2}{c_3^2}l_{33} \qquad \text{(A.7.9)}$$

Similarly /

Similarly

$$l_{11} = L_{11} - 2.\frac{c_1}{c_4} L_{14} + \frac{c_1^2}{c_4^2} L_{44} \qquad \text{(A.7.10)}$$

$$l_{12} = L_{12} - \frac{c_2}{c_4} L_{14} - \frac{c_1}{c_4} L_{24} + \frac{c_1 c_2}{c_4^2} L_{44} \qquad \text{(A.7.11)}$$

$$l_{22} = L_{22} - 2\frac{c_2}{c_4} L_{24} + \frac{c_2^2}{c_4^2} L_{44} \qquad \text{(A.7.12)}$$

$$l_{13} = \frac{c_1 c_3}{c_4^2} L_{44} - \frac{c_3}{c_4} L_{14} \qquad \text{(A.7.13)}$$

$$l_{23} = \frac{c_2 c_3}{c_4^2} L_{44} - \frac{c_3}{c_4} L_{24} \qquad \text{(A.7.14)}$$

$$l_{33} = \frac{c_3^2}{c_4^2} L_{44} \qquad \text{(A.7.15)}$$

APPENDIX A.8

CALCIUM CHLORIDE

C	M	EQV COND	T+	D(V)*.5	1+M*DLNGAMA/DM
0.0000	0.000000	135.86	0.4360	1.3550	1.0000
0.0010	0.001000	128.20	0.4350	1.2940	0.9631
0.0100	0.010011	115.60	0.4200	1.2190	0.9008
0.0500	0.050158	102.46	0.4040	1.1230	0.8376
0.1000	0.100462	92.00	0.3870	1.0910	0.8250
0.2000	0.201430	84.40	0.3540	1.0760	0.8486
0.3000	0.302907	80.45	0.3260	1.0860	0.8960
0.5000	0.507714	75.49	0.2890	1.1290	1.0205
0.7000	0.714645	67.69	0.2710	1.1780	1.1653
1.0000	1.029642	60.89	0.2590	1.2430	1.3886

SQRT S *10	L11/N *10+12	L12/N *10+12	L22/N *10+12	F12	Q12
0.0000	1.6109	0.0000	8.2528	0.0000	0.0000
0.5477	1.5547	0.1147	8.0088	0.1270	0.0325
1.7321	1.4574	0.3075	7.8161	0.3380	0.0911
3.8730	1.3545	0.4861	7.5308	0.5369	0.1522
5.4772	1.2591	0.6063	7.2695	0.6819	0.2004
7.7460	1.1365	0.6686	7.1930	0.7843	0.2338
9.4868	1.0445	0.6806	7.1849	0.8352	0.2485
12.2474	0.9131	0.6547	7.0740	0.8802	0.2576
14.4914	0.8132	0.6413	6.5823	0.9435	0.2772
17.3205	0.7115	0.5762	5.9982	0.9573	0.2789

SQRT S *10	NR11 *10-11	-NR12 *10-11	NR22 *10-11	Q10	Q20
0.0000	6.2073	0.0000	1.2117	0.7494	0.6621
0.5477	6.4388	0.0922	1.2499	0.7408	0.6473
1.7321	6.9190	0.2722	1.2901	0.7310	0.6129
3.8730	7.5579	0.4879	1.3594	0.7205	0.5755
5.4772	8.2744	0.6901	1.4332	0.7147	0.5421
7.7460	9.3077	0.8652	1.4707	0.7252	0.4999
9.4868	10.2038	0.9666	1.4834	0.7391	0.4688
12.2474	11.7296	1.0856	1.5141	0.7612	0.4306
14.4914	13.3209	1.2977	1.6456	0.7661	0.4051
17.3205	15.2396	1.4639	1.8078	0.7737	0.3926

SQRT S *10	-R10 *10-9	-R20 *10-9	-COR10 *10-11	-COR20 *10-11	ROO/N *10-7
0.0000	5.6079	2.1892	3.1039	1.2117	9.0214
0.5477	5.8342	2.1689	3.1272	1.2038	8.9833
1.7321	5.7432	2.0813	3.1873	1.1540	8.9370
3.8730	5.9476	2.0158	3.2911	1.1154	9.0172
5.4772	6.2387	1.9693	3.4471	1.0881	9.2095
7.7460	6.8741	1.8835	3.7887	1.0381	9.6534
9.4868	7.5219	1.8191	4.1353	1.0001	10.1498
12.2474	8.7426	1.7768	4.7792	0.9713	11.2466
14.4914	9.8631	1.8333	5.3627	0.9968	12.4417
17.3205	11.4186	1.9955	6.1559	1.0758	14.2917

```
begin comment Tracer diffusion program
      integer n,f;
      f:=Format ( ( sss-d.dddd10-nd) );
      open (2C);        open(7C);
start:copytext (2C,7C, ( ; ) );
      n:=read (2C);
      begin integer i,qq,h;
            real sx,sy,sxy,sx2,sy2,m,c,d,dy,dm,vo,
                 a,nn,avinc,t12,t;
            array x,y,yy,yc,e,corr, (1:n),inc(2:n), s(1:9);
            boolean array duff (1:n);
            boolean nohold, decay, ante, decapo;
            nohold:=decay:=false;
            sx:=read (2C);
            sy:=read (2C);
            ante:=if sx=sy then false elsetrue;
            if ante then sy:=sy-sx;
            for i:=1 step 1 until n do
            begin    x (i):=read (2C);
                    yy (i):=read (2C);
                    yy (i):=yy(i)- sx;
                  duff (i):=false;
            end;
            vo:=read (2C);
            nn:=read (2C);
             a:=read (2C);
            if ante then for i:=1 step 1 until n do
            begin yy (i):=yy(i)-sy;
                  sy:=syx(1-a/(vo-ix(nn-a)))
```

```
            end;
            if in basic symbol (2C)≠ 152 then decay:=true;
            for i:=1 step 1 until 9 do s(i):=read (2C);
            if in basic symbol (2C)=12 then nohold:=true;
            if a=C.C then
            writetext (7C , (( 4C ) SIMPLE*WITHDRAWL*SAMPLING( 2c )) )
            else
            writetext (7C,(( 4C ) WITHDRAWL/ADDITION*SAMPLING( 2c )) );
            if decay then
            begin t 12:=read (2C);
                    t:=read (2C);
                  for i:=1 step 1 until n do
                  yy(i):=yy(i)/exp(-C.693/t12x(i-1)xt)
            end;
total;      for i:=1 step 1 until ndo y(i):=yy(i);
            writetext (7C,((2c)*INTERVAL(1CS)INC(2C)));
            sx:=sx2:=C.C;    qq:=C;
            for i:=2 step 1 until n do
            if not (duff(i) or duff(i=1)) then
            begin inc (i):=(y(i)x(vo-(i-1)x(nn-a))-y(i-1)x
                  (vo-(i-1)x(nn-a)-a))/(X(I)-x(i-1))/vo;
                  write (7C,format((ssdd)),i-1;
                  out basic symbol (7C,161);
                  write (7C,format((dd)),i);  space(7C,6);
                  write (7C,f,inc(i));   newline(7C,1);
                  sx:=sx+inc(i);
                  qq:=qq+1;
            end;
            avinc:=sx/qq;
            for i:=2 step 1 until n do
```

```
        sx2:=sx2+(if not (duff(i) orduff (i-1)) then
         (avinc+inc (i))↑2 else C.C);
        dm:=sqrt(sx2/(qq-1));
        writetext(7C,((c) AVERAGE*INC*=));
        write(7C,f,dm);
        corr(1):=C.C;
        for i:=2 step 1 until n do corr(i):=axy(i-1)/
        (vo-(i-1)x(nn-a)) -avinc x (x(i)-x(i-1))x(i-1)x
        (nn-a)/(vo-(i-1)x(nn-a))+corr(i-1);
        for i:=1 step 1 until n do y (i):=y(i)+corr(i);
leastsq: sx:=sy:=sxy:=sx2:=sy2:C.C;      h:=C;
        for i:=1 step 1 until n do ifnot duff(i) then
        begin sx:=sx+x(i);
              sy:=sy+y(i);
             sxy:=sxy+x(i) xy(i);
             sy2:=sy2+y(i)↑2;
             sx2:=sx2+x(i)↑2;
               h:=h+1;
        end;
        d:=hxsx2-sx 2
        m:=(hxsxy-sxxsy)/d;
        c:=(sx2xsy-sxxsxy)/d;
        for i:=1 step 1 until n do
        if not duff (i) then yc(i);=mXX(i)+c;
        dy:=sy2+hxc 2+m 2xsx2-2x(cxsy+mxsxy-mxcxsx);
        dm:=sqrt(hxdy/(h-2)/d);
         d:=sqrt(dyxsx2/(h-2)/d);
        for i:=1 step 1 until n do
        if not duff (i) then e(i):=y(i)-yc(i);
        writetext(7C,((4c)M*=));      write(7C,f,n);
```

```
writetext(7C,((3s) STANDARD*DEVIATION*IN*M*=) );
write (7C,f,dm);
writetext (7C,((2c) C*=) );
write(7C,f,c);
writetext(7C,(( 3s) STANDARD*ERROR*IN*C*=) );
write (7C,f,d);
writetext (7C,(( 2C ) RMS*ERROR*IN*Y*=) );
write (7C,f,sqrt(dy/(h-2)));
writetext (7C,(( 3c5s )Y*INIT( 9s ) CORR( 1Cs )Y*CBS( 8s )
Y*CALC ( 7s ) DEVIATION ( 2C ));
for i:=1 step 1 until n do if not duff (i) then
begin write (7C,f,  yy(i));
      write (7C,f,corr(i));
      write (7C,f,   y(i));
      write (7C,f,  yc(i));
      write (7C,f,   e(i));   newline (7C,1);
end;
d:=mxvoxs(1)xs(2)/(s(4)xs(5)x6C);
writetext (7C,((2C) DIFFUSION*COEFF*D1A* =**) );
write (7C,f,d);
if not nohold then
begin writetext (7C,((2c)HOLD*UP*TIME*(MIN)*=**) );
write (7C,f,-c/m);
writetext (7C,((2C) HOLD*UP*TIME*DIFF*COEFF*=**) );
    write (7C,f,-s(2)↑2xm/(cx360));
end;
dm:=C.11733xsqrt(s(9)x5.29xs(7)/s(8))x
    (s(8)xs(6)↑2/s(7))↑(1/3);
writetext (7C,((4c)SCATTERGOOD/LIGHTFOOT*CORRECTION(2c)
MASS*TRANSFER*COEFF*=**) );
```

```
            write (7C,f,dm);
            writetext (7C,((2C)DIFFUSION*COEFF*D1*=**) );
            write (7C,f,d/(1-(2xdxs(3)/(s(2)xdmxs(1)))));
again:      if in basic symbol (2C)=12 then goto newdata;
            dacapo:=readboolean(2C);
            if in basic symbol (2C)= 152 then for i:=read(2C)
            while in basic symbol (2C) ≠ 13 do duff (i):=true;
            if dacapo then writetext (7C,(( 6c )TOTAL*) ) else
            writetext(7C,(( 6c) LEAST*SQUARE*) );
            writetext(7C,(RECALCULATION*OMITTING*POINTS) );
            for i:=1 step 1 until n do
            if duff (i) then write (7C,format ((snd)),i);
            newline (7C,2);
            if dacapo then goto total else goto leastsq;
newdata:    if in basic symbol (2C) = 142 then goto start;
            close (2C);    close (7C)
            end→
```

```
begin comment Non steady state Fickian diffusion program;
      integer f,o,p;
      real e;
      f:=format ([5s-d.dddd10-nd]);
      e:=ln(10.0);
      open (20);        open (70);
again:  copytext(20,70, ( ; ) );
      p:=read (20);
      o:=read (20);
      begin integer i,m,ma,mc,md;
            real vo,nn,a,sx,sy;
            array ab,or,orc,err(1:o);
            boolean skip,dil,first;
            first:=true;
            skip:=if in basic symbol (20)=152 then
                  false else true;
            if skip then
            begin sx:=0.0;
                  goto intake
            end;
            sx:=read (20);
            sy:=read (20);
            dil:=if sx=sy then false else true;
            if dil then sy:=sy-sx;
intake:     for i:=1 step 1 until o do
            begin ab(i):=read(20);
                  or(i):=read(20);
                  or(i):=or(i)-sx
            end;
            if skip then goto fit;
```

```
            vo:=read(2C);
            nn:=read(2C);
             a:=read(2C);
            if dil then for i:=1 step 1 until o do
            begin or (i):=or(i)-sy
                  sy:=syx(1-a/(vo-ix(nn-a)))
            end;
            writetext(7C,((2cs)INTERVAL( 1Cs )TOTAL*INC ( 2c )) );
            for i:=2 step 1 until o do
            begin err (i):=((or(i)-or(i-1))x(vo-(i-1)x(nn-a))+
                           axor(i-1))/vo;
                  write(7C,format((ssdd)),i-1);
                  out basic symbol(7C,161);
                  write(7C,format((dd)),i);
                  space(7C,6);
                  write(7C,f,err(i));     newline(7C,1)
            end;
            orc(1):=C.C;
            for i=2 step 1 until o do orc(i):=axor(i-1)/
            (vo-(i-1)x(nn-a))-err(i)x(i-1)x(nn-a)/(vo-(i-1)x
            (nn-a))+orc(i-1);
            fori:=1 step 1 until o do or (i):=or(i)+orc(i);
            writetext (7C,((2c)POINT(1Cs)VOL*CORR(2C)) );
            for i:=1 step 1 until o do
            begin write(7C,format((ssdd)),i);      space(7C,5);
                  write(7C,f,orc(i));      newline(7C,1)
            end;
fit:  m:=p+1;
      ma:=p;
      mc:m+1;
```

```
md:=mx2-1;
 begin integer j,k,l,n,mn,ka,mb,am;
       real ans,bans,b,in,q;
       array c,d(1:m,1:m),t,x(1:m),detr(1:mc),keep(1:md);
       procedure ASSIGN(n);
       value n;
       integer n;
       begin mn:=n+1;
             fori:=1 step 1 until n do
             begin j:=mn-i;
                   if i≤m and j≤m then c(i,j):=keep(n)
             end;
       end ASSIGN;
       for i:=1 step 1 until m do   t(i):=C.C;
       for i:=1 step 1 until md do keep(i):=C.C;
       for i:=1 step 1 until o do
      begin in:=1.C;
             for j:=1 step 1 until md do
             begin keep (j):=keep(j)+in;
                   if j≤m then t(j):=t(j)+or(i)xin;
                   in:=inxab(i)
             end
       end;
       for k:=1 step 1 until md do ASSIGN(k);
      ans:=C.C;
      for i:=1 step 1 until m do ans:=ans+(if c(i,i) C.C
      then ln(c(i,i))/e else if c(i,i)=C.C then C.C
      else ln(abs(c(i,i)))/e;
      am:=m;
      ans:=ans/am;
      bans:=1C.C↑ ans;
```

```
for i:=1 step 1 until m do
    begin
    t (i):=t(i)/bans;
    for j:= 1 step 1 until m do
    c(i,j) := c(i,j)/bans;
    end;
for j:= 1 step 1 until mc do
    begin
    for i:= 1 step 1 until m do
    for k:= 1 step 1 until m do
    d(k,i):= c(k,i);
    b:= 1.C;
    mb:= j-1;
    if mb≠C then for k:=1 step 1 until m do
    d(k,mb):= T(k);
for k:=1 step 1 until ma do
        begin
        ka:=k+1;
        if d(k,k)=C.C then goto P86
    P8C:  b:= d(k,k)xb;
        q:= d(k,k);
        for l:= k step 1 until m do d(k,l):= d(k,l)/q:
        for l:= ka step 1 until m do
        begin
        a:= d(l,k);
        for n:= k step 1 until m do
        a(l,n):= d(l,n)-d(k-n)xa;
        end;
    for l:= ka step 1 until m do d(K,L):=C.C
    goto out;
```

```
P86: for i:= ka step 1 until m do if d(k,i)≠C.C then
     begin
     b:= -b;
     for l:= k step 1 until m do
     begin
     in:= d(l,k);
     d(l,k):=d(l,i);
     d(l,i):= in;
     end;
     goto P8C;
end;
detr(j):=C.C;
goto fin;
out: end;
detr(j):=d(m,m)xb;
fin: end;
for j:= 2 step 1 until mc do x(j-1):=detr(j)/detr(1);
writetext(7C,(( 2C ) ORDER*OF*IT*=*) );
write(7C,format( ( dd ) ),p);
writetext(7C, (( 4C )POWER*OF*A ( 5s )COEFFICIENT ( 2c )) );
for i:= 1 step 1 until m do
begin write(7C,format( (ssssdd) ), i-1);
      space(7C,4);
      write(7C,f,x(i) );
      newline(7C,1)
end;
for i:= step 1 until o do
begin orc(i):=x(m);
       for j:= ma step-1 until 1 do orc(i):= x(j)+
       orc(i)xab(i);
```

```
                err(i):= or(i)-orc(i)
        end;
        writetext(7C,(( 2c6s )ABSCISSA ( 11s )ORDINATE ( 11s )
        CALC*ORDINATE ( 11s )DEVIATION ( 2c )) );
        for i:= step 1 until o do
        begin write(7C,f,ab(i));     space(7C,3);
              write(7C,f,or(i));     space(7C,3);
              write(7C,f,orc(i));    space(7C,8);
              write(7C,f,err(i));    newline(7C,1);
        end;
              if not first then
              begin sy:= x(2);   goto finale
              end;
              for i:= 1 step 1 until o do
              begin err (i):= x(m)x(m-1);
                    for j:= ma step -1 until 2 do
                    err(i):= x(j)x(j-1)+err(i)xab(i);
                    or(i):= ln(err(i)xsqrt(ab(i)));
                    ab(i):= 1/ab(i)
              end
        end;
        p:= 1;
        first:= false;
        writetext(7C, ((4C)ORDINATE*IS*NOW*LN(DP/DTxT C.5) (c)
        ABSCISSA*IS*NOW*1/T (4c)) );
        goto fit;
finale: sx:= read(2C);
        sx:= sxxsx;
        writetext(7C,((6c)DIFFUSION*COEFFICIENT*(CM2SEC-1)*=*) )
        write(7C,f,-sx/(syx24C));
```

```
        end;
        if in basic symbol(2C)=142 then goto again;
        close (2C);     close(7C)
end→
```

```
begin comment Transport numbers from self diffusion flux
              and flux with or against the current;
      integerz,l,f;
      real ta,tb,tc,amp,jo,jg,c,d,ratio,x;
      boolean with bar;
     f:= format ((sss-d.dddd10-nd));
     open(2C);   Ooen(7C);
start: copytext(2C,7C,(;)0;   inbasic symbol(2C);
     if in basic symbol(2C)=152 then with:= true else with:=false;
     bar:= false;
       z:= read(2C);
     amp:= read(2C);
       c:= read(2C);
       d:= read(2C);
      jo:= read(2C);
      jg:= read(2C);
      tg:= read(2C);
       l:= read(2C);
       x:= if in basic symbol(2C)=152 then 1.C10-3 else read (2C);
      jo:= joxc/d;
      jg:= jgxc/d;
       c:= 9.64910 4xzxjo/amp;
       d:= amp/z/jg/9.64910 4;
      if with then ta:= 1/d else ta:= if in basic symbol(2C)=152
     then read(2C) else1.C;
     tb:= C.C;
     writetext(7C, ((cc)CYCLE(3s)T*GIVEN(7s)T*CALC(8s)RATIO(cc)) );
       z:= C;
loop:  if z=1 then goto stop;
       z:= z+1;
```

```
      if with then
      begin tc:= -cxln(1-dxtg);
         ratio:= tg/tc;
      end else
      begin tc:= cxln(1+dxtg)
         ratio:= tc/tg;
      end;
      write (7C,format((ssdd)),z);
      write (7C,f,tg,);
      write (7C,f,tc);
      write (7C,f,ratio);
      newline(7C,1);
retest: if abs(ratio-1.C)<x then gotoout;
     if ratio>1.C then tb:= tg else ta:= tg;
     tg:= (ta+tb)/2;
     goto loop;
stop: writetext(7C,{(cc) NOT*CONVERGENT*WITHIN*CYCLE*LIMIT(cc)) );
      goto fin;
out: if bar then goto fin;
     x:= x/1C;
     bar:= true;
     l:= l+l;
     writetext(7C(DISCRIMINATION*INCREASED*BY*TEN(c)) );
     goto retest;
fin: if in basic symbol(2C)=142 then
     begin bar:=false;   goto start
     end;
     close(2C);   close(7C);
end→
```

```
begin comment This program reads n sets of concn, molality/
density, equivalent conductivity, transport numbers, diffusion
coefficients and activity term and it calculates Onsager L and
R coefficients and three degrees of coupling and outputs the
results in tabular form;
      integer r, r1, r2, n, z, z1, z2, f, md, i, DV;
      real  R, F, T, M, q;
      open(20);     DV:=read(20);     open(DV);
      f:= format( -nddd.dddd );  copytext ( 20, DV, ;; );
      repeat: R:= read (20); F:= read(20); T:= read(20);
      again:  copytext(20, DV, : );
              M:= read (20); r1:= read (20); r2:= read(20);
      z1:=read(20); z2:=read(20);  r:= r1+r2;
       z:=read(20);  n:=read(20); md:=read(20);
begin array c, d, m, t1, lda, D, l11, l22, l12, R11, R22, R12,
      R10, R20, R00, F12, x, y, act 1:n ;
      for  i:= 1 step 1 until n do begin
      c i  :=read(20);  d i  :=read(20);  lda i  :=read(20);
      t1 i :=read(20);  D i  :=read(20);  act i  :=read(20);
      end;
      q :=10 8xR
```

```
0;→
DD380+Z030103RSST→

begin   comment  This program reads n sets of concn,
        molality/density, eqivalent conductivity,
        transport numbers, diffusion coefficients
        and activity term and it then calculates
        Onsager L and R coefficients and three degrees
        of coupling and outputs the results in tabular
        form;
           integer r, r1, r2, n, z, z1, z2, f, md, i, DV;
      real    R, F, T, M, q;

open(20);        DV:=read(20);          open(DV);
 f:=format([-nddd.dddd]); copytext(20, DV, [;;]);
repeat: R:=read(20);  F:=read(20);  T:=read(20);
again:  copytext(20, DV, [:]);
        M:=read(20);  r1:=read(20);  r2:=read(20);
 z1:=read(20);         z2:=read(20);  r:=r1+r2;
   z:=read(20);  n:=read(20);  md:=read(20);
begin array c, d, m, t1, lda, D, l11, l22, l12, R11,
      R22, R12, R10, R20, R00, F12, x, y, act [1:n];
for i:= 1 step 1 until n do begin
c[i]:=read(20);   d[i]:=read(20); lda[i]:=read(20);
t1[i]:=read(20);   D[i]:=read(20);   act[i]:=read(20)
end;
q:=10↑8×R×T×r×r1×z1;
for i := 1 step 1 until n do  begin
x[i]:=D[i]/(q×act[i]);  y[i]:=lda[i]/(1000×F↑2);
if md = 3 then m[i] := d[i] else
 m[i]:=c[i]/(d[i]-0.001×c[i]×M);

l11[i]:=y[i]×t1[i]↑2/z1↑2+r1↑2×x[i];
if c[i]=0.0 then l12[i]:=0.0 else
 l12[i]:=y[i]×t1[i]×(1-t1[i])/(z1×z2) + r1×r2×x[i];
l22[i]:=y[i]×(1-t1[i])↑2/z2↑2+r2↑2×x[i];
x[i]:=l11[i]×l22[i]-l12[i]↑2;
R11[i]:=l22[i]/x[i];
R12[i]:=-l12[i]/x[i];   F12[i]:=-R12[i]×y[i];
R22[i]:=l11[i]/x[i];
if md = 3 then  begin  if c[i] = 0.0 then x[i] :=0.01807/z
 else x[i] := 18.015×m[i]/( 1000 × z × c[i]) end
           else   x[i]:= 18.015/(z×(1000×d[i]-M×c[i]));
R10[i]:=-(r1×R11[i]+r2×R12[i])×x[i];
R20[i]:=-(r1×R12[i]+r2×R22[i])×x[i];
R00[i]:=-(r1×R10[i]+r2×R20[i])×x[i]    end;     test(0);



writetext(DV, [ [11s]c[8s]m[7s]Eqv*Cond[6s]t+[5s]D(v)10^5[s]
                        1+m×d1nGama/dm[2c] ]);
for i:=1 step 1 until n do begin
space(DV, 5);
 write(DV, f, c[i] );
  write(DV, format([ndd.dddddd]), m[i]);
   write(DV, format([-ssnddd.dd]), lda[i]);
    write(DV, f, t1[i]);
     write(DV, f, D[i]);
```

```
        write(DV, f, act[i]); newline(DV, 1); end;


writetext( DV, [ [2c9s]Sqrt*S[4s]111/N[5s]112/N
          [5s]122/N[6s]F12[7s]Q12[c10s]
          x10[7s]₁₀+12[6s]₁₀+12[6s]₁₀+12[2c] 1 );

for i := 1 step 1 until n do begin

space(DV, 5);
 write(DV, f, 10xsqrt( z x c[i] x ( z1 - z2 )/2) );
  write(DV, f, 111[i] x ₁₀12 );
   write(DV, f, 112[i]x₁₀12 );
    write(DV, f, 122[i]x₁₀12 );
     write(DV, f, F12[i]);
      write(DV, f, 112[i]/ sqrt( 111[i]x122[i] ) );
       newline(DV, 1);  end;

writetext( DV, [ [2c9s]Sqrt*S[4s]NR11[6s]-NR12[5s]
          NR22[7s] Q10[7s]Q20[c10s]x10[6s]₁₀-11
         [7s]₁₀-11  [5s]₁₀-11[2c] 1 );

for i := 1 step 1 until n do begin



space(DV,5);
 write(DV, f, 10x sqrt( z x c[i] x (z1-z2)/2 ) );
  write(DV, f, R11[i]x₁₀-11);
   write(DV, f, -R12[i]x₁₀-11);
    write(DV, f,  R22[i]x₁₀-11);
     write(DV, f, -R10[i]/sqrt( R11[i]xR00[i] ) );
      write(DV, f, -R20[i]/sqrt(R22[i]xR00[i]) );
       newline(DV, 1);  end;



writetext( DV, [ [2c9s]Sqrt*S[4s]-R10[6s]
-R20[6s]-COR10[4s]-COR20[4s]R00/N[c10s]
  x10[7s]₁₀-9[7s]₁₀-9[6s]₁₀-11[6s]₁₀-11[8s]₁₀-7[2c] 1 );

for i:= 1 step 1 until n do begin


space(DV,5);
 write(DV, f, 10x sqrt( zx c[i] x (z1-z2)/2 ) );
  write(DV, f, -₁₀-9xR10[i] );  write(DV, f, -₁₀-9xR20[i] );
   write(DV, f, -₁₀-11 xR10[i]/(zx x[i]) );
    write(DV, f, -₁₀-11 x R20[i]/ (zxx[i]) );
     write(DV, f, R00[i]x₁₀-7 );  newline(DV, 1);
end   end;       n:=read(20);
if n = 1 then goto again else if n=2 then goto repeat;
close(20);   close(DV);
end→
```